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**Sampling and Analysis of  
Diesel Engine Exhaust and the  
Motor Pool Workplace Atmosphere**

**Final Report**

March 1, 1988

W. H. Griest, R. A. Jenkins, B. A. Tomkins,  
J. H. Moneyhun, R. H. Ilgner, T. M. Gayle,  
C. E. Higgins, and M. R. Guerin

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Project Officer: James C. Eaton  
Health Effects Research Division  
U.S. Army Biomedical Research  
and Development Laboratory  
Fort Detrick, Frederick, Md 21701-5010

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W. H. Griest, R. A. Jenkins, B. A. Tomkins, J. H. Moneyhun,  
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FINAL REPORT

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## EXECUTIVE SUMMARY

The Department of Defense is concerned that a changeover of mobility fuel sources from petroleum to alternate or synthetic crude oils may be accompanied by a greater or different toxicological hazard to military personnel exposed to fuel-related emissions such as diesel engine exhaust and fuel liquids and vapors. The purpose of this project originally was to compare the organic chemical composition of the exhaust of diesel engines fueled with petroleum and shale oil-derived DF-2. The failure of another DOD contractor to prepare shale oil-derived DF-2 for Army testing and the realization of the current lack of knowledge of the fuel-related contaminants present in the military workplace atmosphere led to a redirection of the focus of this project. The objective was modified to include a detailed organic chemical characterization of diesel engine exhaust and the petroleum-derived diesel fuel-related contaminants in the workplace atmosphere to which military personnel are exposed the most frequently and at the highest levels.

This objective was approached by two sampling and analysis campaigns. The first sampling trip to Fort Carson, CO collected particulate and vapor phase samples of diesel engine exhaust from a variety of vehicles and dynamometer stand-mounted diesel engines. A limited number of diesel fuel, crankcase oil, and workplace atmosphere samples from three motor pool garages also were collected for compositional comparison. The second sampling trip focused upon the collection of workplace atmosphere samples for detailed study. The sampling strategy included multiple locations within three motor pool garages. Both time averaged (TA; 3 to 8 hrs.) and time resolved (TR, 1 to 3 hrs) collections of particulate phase and vapor phase organic compounds were conducted. On-site measurements included total suspended particulates (TSP), particle size distribution, and selected gases. The particulate samples were analyzed in the laboratory for the major chromatographable organic compounds, and selected samples were analyzed for 4- to 6-ring polycyclic aromatic hydrocarbon (PAH) dermal tumorigens. The vapor phase traps were analyzed for major organic constituents, i.e., n-alkanes and alkyl benzenes. Qualitative inventories of organic compounds in the particulate and vapor phases of selected samples were made using GC-MS.

Diesel engine exhaust was found to contain a highly complex mixture of organic compounds, including many fuel and crankcase oil-related components. The composition of the motor pool workplace atmosphere reflected the major contribution of diesel engine exhaust, but a major observation was that the latter is not an accurate chemical surrogate or model for the former, and would not be appropriate as the sole medium for toxicological studies of the former. TSP concentrations in the motor pool workplace atmosphere ranged from 12 to 300  $\mu\text{g}/\text{m}^3$ , and were bimodally distributed with a small particle mode at 0.4-0.5  $\mu\text{m}$  (mass median aerodynamic diameter, MMAD) and a large particle mode at 3-4  $\mu\text{m}$  (MMAD). Total  $\text{C}_1\text{-C}_6$  hydrocarbons ranged over 4 to 7 ppm. The

major chromatographable particulate organic compounds were a series of n-alkanes ranging from  $C_{12}$  to at least  $C_{33}$  at levels up to  $37 \text{ ng/m}^3$  (corresponding to  $190 \text{ } \mu\text{g/g}$  in the TSP) in the most contaminated motor pool surveyed in this study. The PAH in that motor pool also were relatively highly concentrated. Benzo[a]pyrene (BaP) was present at  $13 \text{ ng/m}^3$  (or  $65 \text{ } \mu\text{g/g}$  in the TSP). The major chromatographable organic vapor phase compounds were a series of n-alkanes from  $C_3$  to at least  $C_{16}$ , benzene, and benzenes with alkyl-substitution to  $C_4$ . Benzene and toluene were determined at ca. 6 and  $45 \text{ } \mu\text{g/m}^3$ , respectively, in one motorpool. The concentrations of organic compounds in the workplace atmosphere were found to vary by factors of ca. 2 to 7 at a single location or among different locations within the same motor pool. A somewhat greater variability was observed from motor pool to motor pool. The highest variability was in the trace level constituents such as BaP, where factors ranged up to ca. 50.

This characterization provides an important input for health risk assessment and for the design of animal toxicology studies of the fuel-related contamination in the workplace atmosphere from current petroleum-derived diesel fuel. It also provides a database for comparison with future studies of atmospheric contamination from alternate or synthetically-derived mobility fuels.

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## INTRODUCTION

Considerable questions remain regarding the potential toxicity of diesel engine exhaust to humans (1-3), although the presence in diesel engine exhaust of toxic, mutagenic, and carcinogenic compounds is well-documented (1,4). Extracts of particulate matter from diesel engine exhaust have been found to exhibit mutagenic activity, and high concentrations of diesel exhaust particulate matter have induced lung cancers in inhalation studies with rats (2).

The Department of Defense is concerned that a changeover of fuel sources from petroleum to alternate or synthetic crude oils might be accompanied by an increase or change in the nature of the fuel-related health hazards to military personnel. Such concerns are justified from reports (e.g., 5,6) that toxic compounds (e.g., PAH) in diesel fuel (DF) are carried over into the engine exhaust, and compositional differences exist (7-9) between petroleum- and synthetically-derived mobility fuels. The mutagenic emissions from a diesel engine have been reported (10) to be greater for a shale oil-derived marine diesel fuel (DFM) than for a petroleum-derived DF-2.

The original objective of this project was to characterize the organic chemical composition of diesel engine exhaust from military vehicles fueled on petroleum-derived DF-2 at Fort Carson, CO, and to compare the exhaust composition with that from the same vehicle types and under the same operating conditions after the entire post had converted to a shale oil-derived DF-2. However, the DOD contractor which was to provide hydrotreated shale oil for refining into DF-2 and other mobility fuels experienced severe difficulties with their oil shale retort, and the shale oil was not produced. Because of this difficulty and the realization of the lack of knowledge concerning the exposure of military personnel to exhaust and other fuel-related contaminants, this project was redirected toward a characterization of the organic chemical composition of the workplace atmosphere in which military personnel are exposed to current petroleum-derived fuel-related contaminants the most frequently and at the highest concentrations. This characterization included a comparison with routine industrial hygiene measurements to determine if those atmospheric contaminants covered by regulations could serve to indicate that there is a likely contamination by the trace hazardous constituents with which this study was concerned.

The following sections report the collection and organic chemical characterization of diesel engine exhaust and workplace atmosphere samples from four motor pool garages at Fort Carson, CO. The findings of this project supplemented those of a companion project, "Synthetic and Alternate Fuels Characterization," Army Project Order No. 81PP1813, which focused upon a chemical and toxicological comparison of DF derived from petroleum, shale oil, and tar sands. The results of the latter project are being reported separately (11). Together, the findings will facilitate the risk assessment of a conversion to synthetically-derived or alternate sources of mobility fuels, and the design of exposure conditions for animal toxicology studies of the fuel-related atmosphere contamination.

SAMPLING OF AIRBORNE DIESEL EXHAUST AND THE MOTORPOOL  
WORKPLACE ATMOSPHERE AT FORT CARSON, COLORADO

Sampling Strategy

Because the project had been conceived as a comparison of the compositions of the airborne diesel exhaust entering the workplace atmosphere before and after the projected changeover to shale oil-derived diesel fuel at Fort Carson, Colorado, the primary focus of the first visit was to obtain baseline information on the composition of exhaust generated from the large diesel engines used by the Army. (There exists a considerable body of literature on the composition of exhaust from small, passenger vehicle engines.) With guidance from U.S. Army Biomedical Research and Development Laboratory (USABRDL) project management, a sampling strategy was developed which involved the collection of particulate and vapor phase exhaust samples from idling large vehicles. Idling vehicles were chosen for two reasons. First, the logistics involved with sampling exhausts from vehicles in motion would have required resources beyond those available. More importantly, it was believed that the greatest magnitude troop exposures would occur when the vehicles were stationary. For purposes of comparison, a few exhaust samples would be acquired from vehicle engines being run through dynamometer test cycles. These engines were considered to be in the highest state of tune, and because samples were acquired during a full test cycle, should be more indicative of vehicles actually in motion. A few additional samples were taken of the atmosphere in enclosed vehicle repair bays. This was thought to be an additional exposure medium because the exhaust might undergo considerable aging before it was actually inhaled. A larger number of samples was collected in the field than could be characterized in the laboratory to allow some flexibility in the choice of the best samples for analysis and to provide for later, additional analyses (if necessary) to confirm unexpected observations.

The results obtained from analysis of the workplace atmosphere samples from the first visit formed the impetus for the second visit. It became clear that Fort Carson would not soon be converted to operation on shale oil-derived diesel fuel as originally planned. Also, comparison of the workplace atmosphere samples with the freshly collected exhaust from idling engines indicated that the fresh exhaust had a considerably different composition from that of the workplace atmosphere. Combined with the observation that exhaust levels were much higher in enclosed areas, these findings suggested that the second sampling effort should focus on the determination of the composition of those atmospheres in which the greatest exposures were likely to occur: enclosed workplaces. As in the first sampling expedition, a far greater number of samples were collected than could be fully characterized in this effort.

### Sampling Trips

The first sampling trip was conducted September 19-28, 1984. Actual sample acquisition occurred on September 21 and 24-26. The remainder of time was required for travel, equipment loading and unloading, and sample packaging and shipment. Sampling was conducted at three locations: The civilian-run Building 8000, referred to as the Directorate of Logistics (DOL), the motor pool building of the Fourth Engineering Bn, and the motor pool building of the 4/68th Armored Brigade. Specific details of the sampling equipment are given below. In general, the DOL was the facility where the dynamometer test runs were conducted. In order to acquire exhaust samples from these runs, it was necessary to sample the exhaust stacks on the roof of the building. The logistics of sampling at this location were somewhat complex, since the open end of the stack for the dynamometer used for most of the runs was located approximately 3.5 feet out from the side of the building, and about 10 ft. above the roof level. Flexible aluminum pipe (ca. 4" o.d.) proved to be too flexible to be supported near the exhaust. Thus, it was necessary to make the piping less flexible by fastening aluminum rods to the pipe with duct tape. The sampling arrangement is illustrated in Figure 1. As described below, outside air was mixed with the exhaust such that at no time did the temperature of the stream actually being collected exceed 52°C.

Sampling of the vehicle exhausts was conducted at the individual motor pools where the vehicles were located. Again, flexible aluminum was used to channel the diluted exhaust to the sampling equipment. This is illustrated in Figure 2. Typically, the vehicle would be maintained at idling speed for one hour. Workplace atmosphere samples were collected on the first trip by locating the sampling equipment about head height in each of the two motor pool buildings, usually in the repair bay with the most activity. A typical sampling site is portrayed in Figure 3. Background samples were obtained for the outside ambient air by collecting particulate and vapor phase samples on the upwind side of the roof of the DOL facility.

The samples acquired during this first visit are listed in Table 1.

The second field trip to Fort Carson was conducted over a two week period, from September 21 through October 3, 1986. Samples were actually collected on September 23-26 and September 29 - October 2. On this trip, the samples acquired were predominantly area samples. No direct vehicle exhaust samples were taken, although it was observed that the engine exhaust was the predominant contributor to the samples which were acquired. Three locations were sampled: the wheeled vehicle repair bay of the Division Support Command motor pool (DISCOM), the primary inside overhaul area of the DOL facility, and one of the repair bays of the Fourth Engineering Bn motor pool. Primary attention was given to the DISCOM facility, because it was at this location that particularly high levels of contaminants had been identified in the workplace air in previous industrial hygiene surveys. Three locations were sampled within the DISCOM. A primary sampling location was



Figure 1. Photograph of Equipment Used to Sample Dynamometer Exhausts on Top of DOL Facility

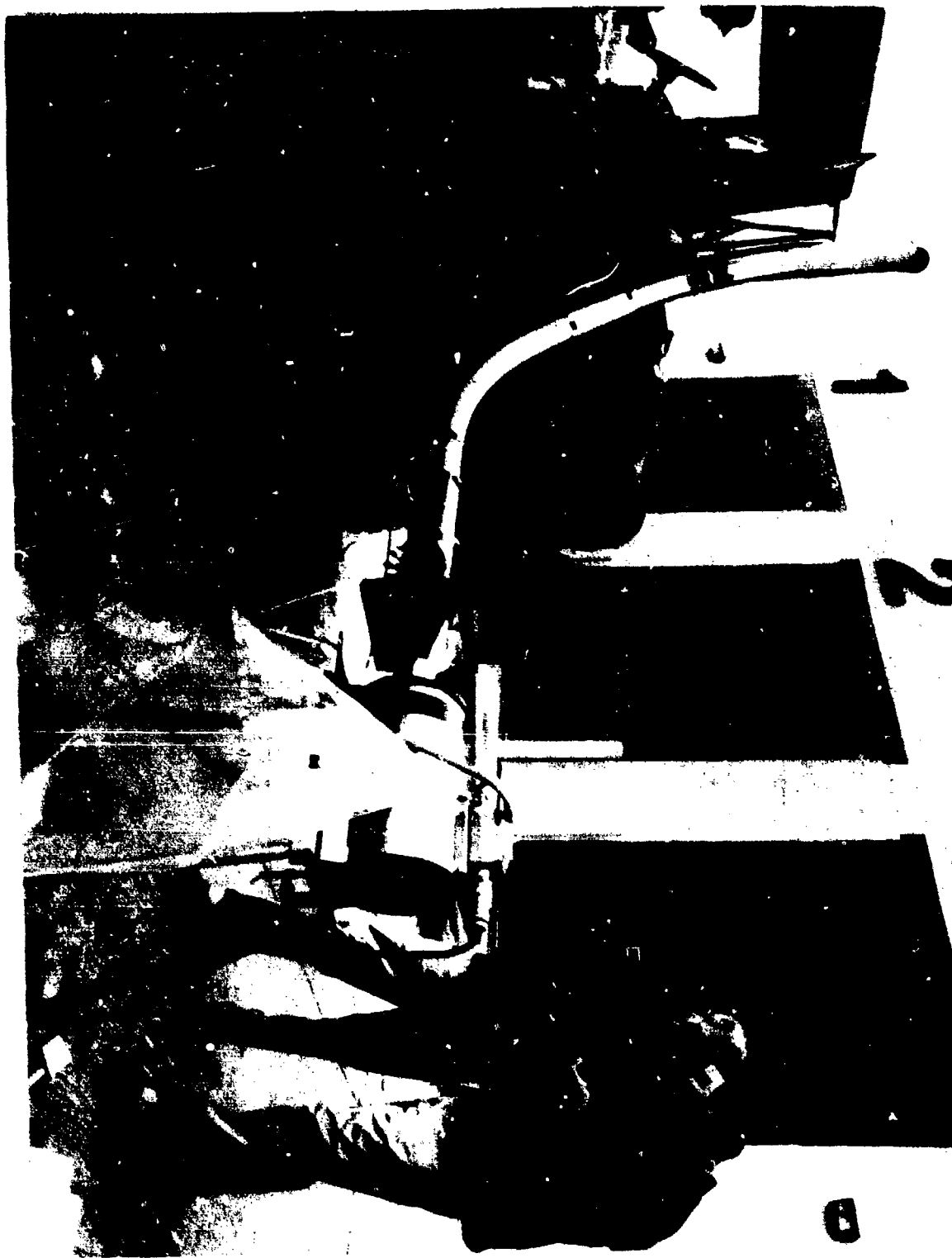


Figure 2. Collection of Diesel Exhaust Samples from Idling 5-Ton Truck at Fort Carson, Co,  
September, 1986

Table 1. Samples Obtained in Fort Carson Expedition September 21-26, 1964

Sample Designation	Description <sup>a</sup>	Hi-Vol Particulates	Membrane Filter	Terix Trap	Gas Bulb	Cascade Impactor	Crankcase Oil	Fuel Sample
21-D-1	Dynamometer-M-60 Engine	X	X	X				
21-D-2	Dynamometer-APC Engine	X	X	X		X		
24-Area E-1	Area-Engineering Mtr. Pool	X		X				
24-E-2	Vehicle-M813 & Eng. Mtr. Pool	X	X	X	X	X		
24-E-3	Vehicle-Truck & Eng. Mtr. Pool	X	X	X	X	X		
24-E-4	Vehicle-Tank Retriever & Eng. Mtr. Pool	X	X	X	X	X		
24-E-5	Vehicle-Chevy Blazer & Eng. Mtr. Pool	X	X	X	X	X		
24-D-1	Dynamometer-Tank Engine	X	X	X	X	X		
24-D-2	Dynamometer-APC Engine	X	X	X	X	X		
25-Area D-1	Area-Top D10 Bld. (Bgnd)	X	X	X	X			
25-A-1	Vehicle-M60 Tank	X	X	X	X	X		
25-Area E-3	Area-Zng. Mtr. Pool	X	X	X	X	X		
25-E-2	Vehicle-Small Bull Dozer	X	X	X	X	X		
25-E-1	Vehicle-APC	X	X	X	X	X		
25-Area A-1	Area-4/68th Armored Mtr. Pool	X	X	X	X	X		
26-Area D-1	Area-Top D10 Bld. (Bgnd)	X	X	X	X			
26-Area A-1	Area-4/68th Ar. Mtr. Pool	X	X	X	X			
26-A-2	Vehicle-2 1/2 Ton Truck	X	X	X		X	X	
26-A-3	Vehicle-GOER Ammo Hauler	X	X	X		X	X	
DF-2-1	DF-2-DIO							X
DF-2-2	DF-2-4/68th Ar. Mtr. Pool							X
DF-2-3	DF-2-Engr. Mtr. Pool							X

<sup>a</sup>APC = armored personnel carrier

M60 = M-60 tank

Bgnd = "background" ambient air sample



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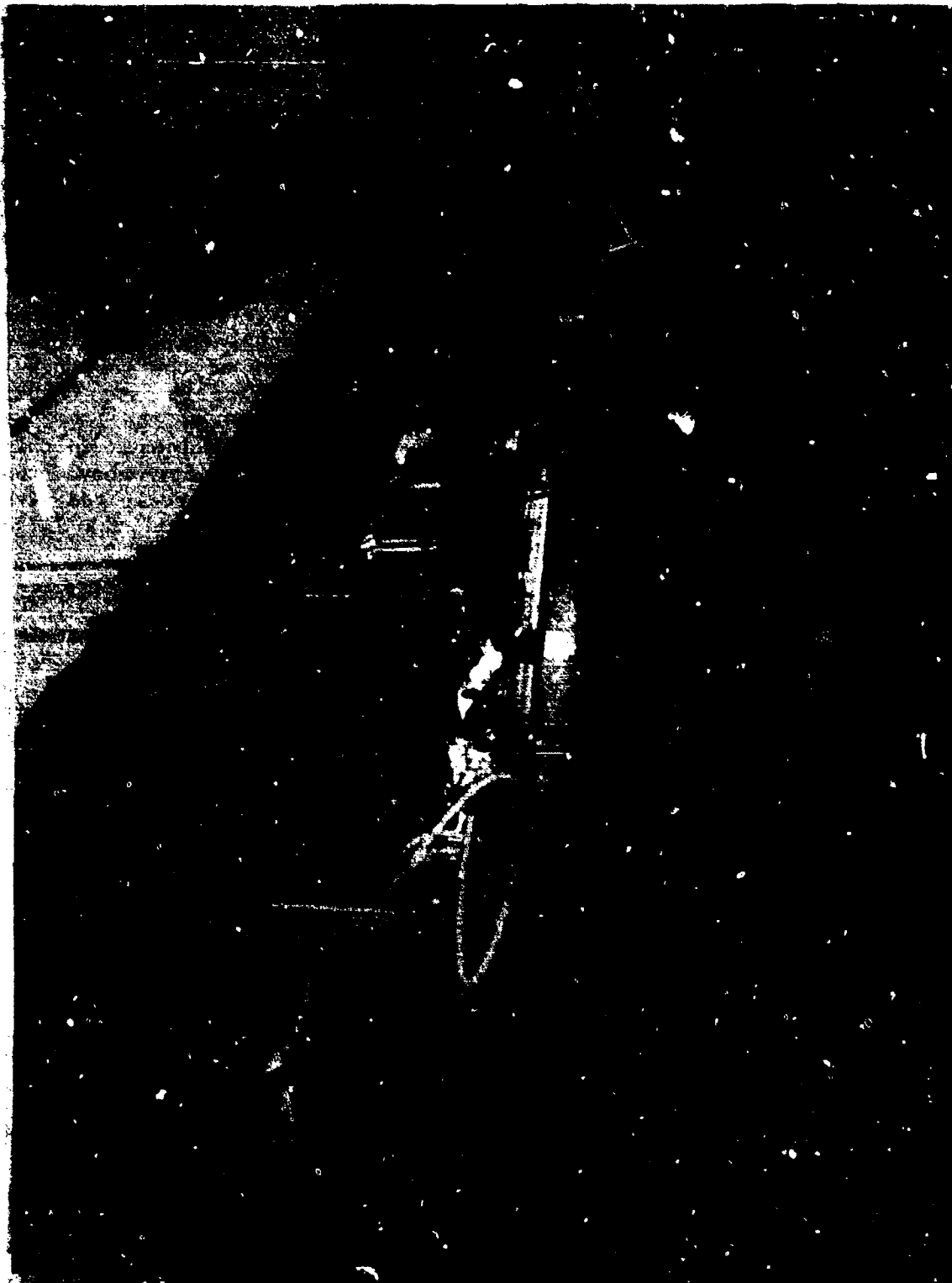


Figure 3. Collection of Workplace Air Samples Inside the 4/68th Armored Brigade Motor Pool Equipment Repair Bay Fort Carson, CO, September, 1984

established about halfway across the width of the south side of the repair bay, near the central support partitions. At this "mid" location, both short duration, so-called "time resolved" sampling, and the longer term, "time averaged" sampling was conducted. The time averaged sampling station consisted of a Staplex High volume sampler for particulates, and a large volume vapor collection system, the core of which was a large Tenax cartridge. The time resolved station consisted of a heavier duty high volume particulate collector, a low volume vapor collection apparatus, which used a triple sorbent cartridge backed with a Tedlar gas sampling bag, and a real time continuous electrochemical carbon monoxide (CO) monitor. In addition, a cascade impactor was used intermittently to collect samples for particle size determination. The sampling equipment was located about 5.5 ft above the surface of the floor. This central sampling station is depicted in Figure 4. In the south-west corner of the repair bay and on the top of an inside roof at the east end of the repair bay (referred to as the mezzanine level), about 20 ft above the level of the main floor were located time averaged sampling stations. In this case, the sampling equipment was located about 3 ft. above the supporting surface, and, the time averaged samples were collected with the Staplex high volume particulate sampling systems and the large Tenax vapor phase sampling cartridges.

Time resolved and time averaged sampling was also conducted in the Fourth Engineering Bn motor building. Both repair bays (designated north and west) were sampled. In these cases, one set of time averaged and time resolved samples were acquired on one side of the bay, while a time averaged sample series was acquired across from the first set of samplers. At the DOL facility, only time averaged samples were acquired. One set were acquired from a position located on top of a small storage building located on the west central location of the main floor, about 15 ft. above the level of the main floor. The other set was taken near the middle of the main floor. In both cases, the sampling equipment was positioned about 2.5 ft. above its base of support. In order to obtain background samples which were representative of the outside air, time averaged samples were acquired immediately outside the west side of the DOL facility. All samples acquired on this sampling expedition are listed in Table 2.

It should be noted that on the second trip, simultaneous sampling was conducted by the staff of the Army Environmental Hygiene Agency. Most samples taken were of the conventional industrial hygiene type. Ms. Susan McGlothlin coordinated those efforts. Results from that effort have been published by the Army (36), and will not be discussed in this report.

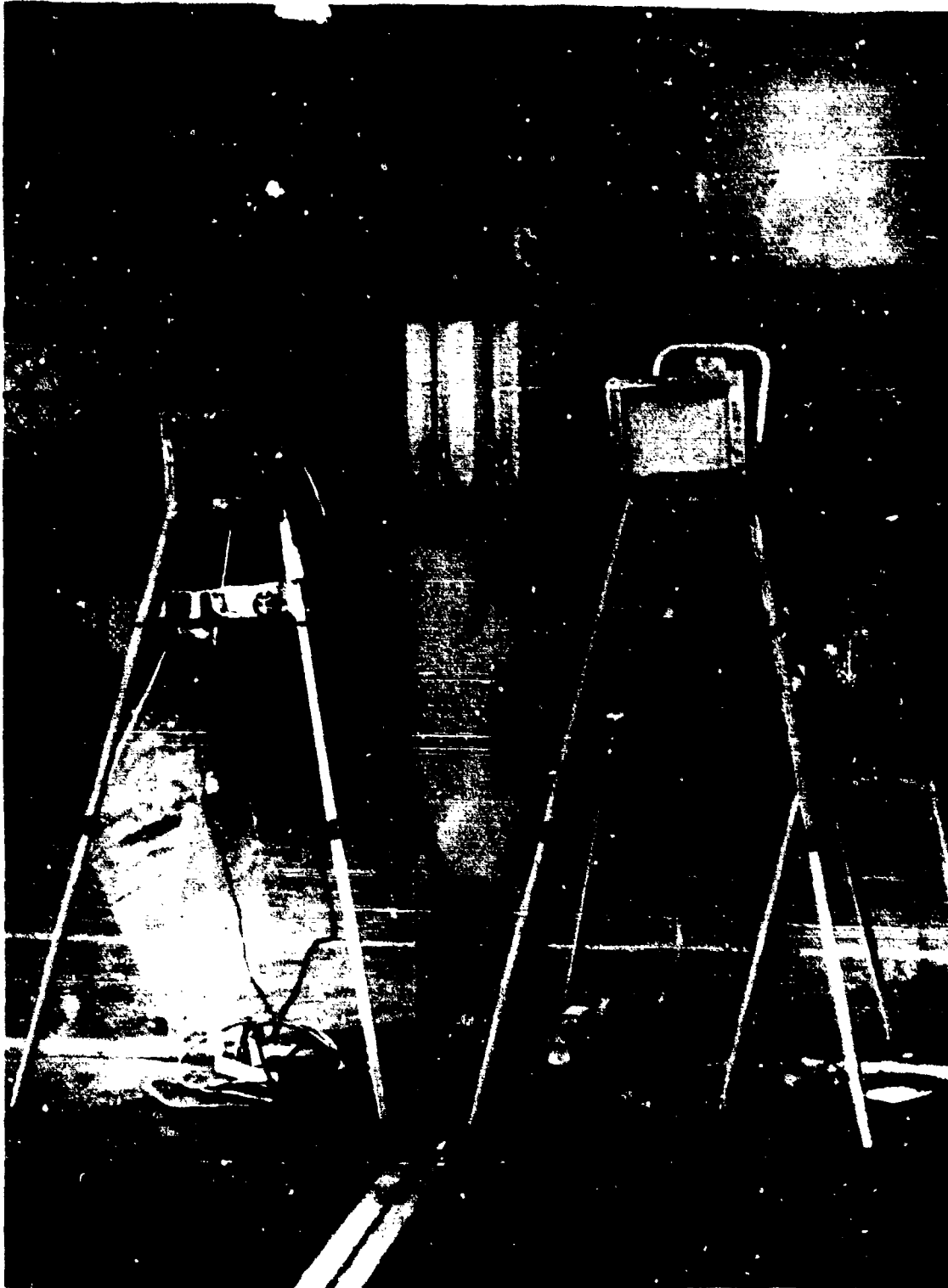


Figure 4. Central ("Mid") Sampling Station on the Floor of the Wheeled Vehicle Repair Bay of the DISCOM Facility, Fort Carson, CO, September, 1986. Time Averaged Samples are Being Collected by the Sampling Equipment to the Left of the Pillar. Time Resolved Samples are Being Collected by Equipment to the Right of the Pillar.

Table 2. Particulates, Vapor, and Gasoline Hydrocarbon Sample by Date  
Fort Carson, Colorado, September 23 - October 1, 1968

PARTICULATES				VAPORS									
MOTOR POOL	DATE	SAMPLING PERIOD		SAMPLING LOCATION	SAMPLING PERIOD		FLOW RATE, ml/min	PARTICLES, mg/filter	SAMPLING VOLUME, cu	PART. MATTER CONC., ug/cu	TOTAL CHCS EC, ppm		
		SAMPLE NUMBER	START		STOP	SAMPLE NUMBER						START	STOP
DIRCON	09/23/68	918-23-TA-1	09:17 AM	10:10 AM	MIDSOLE	918-23-TA-1	09:07 AM	10:10 AM	195	36	147	245	4.6
		918-23-TA-2	10:31 AM	11:31 AM	MIDSOLE	918-23-TA-2	10:31 AM	11:31 AM	195	32	142	225	4.9
		918-23-TA-3	11:40 AM	12:42 PM	MIDSOLE	918-23-TA-3	11:40 AM	12:42 PM	195	18	147	109	5.1
		918-23-TA-4	12:55 PM	01:52 PM	MIDSOLE	918-23-TA-4	12:55 PM	01:52 PM	195	24	135	170	6.3
		918-23-TA-5	01:50 PM	02:50 PM	MIDSOLE	918-23-TA-5	01:50 PM	02:50 PM	195	37	142	190	6.4
		918-23-TA-6	03:00 PM	04:14 PM	MIDSOLE	918-23-TA-6	03:00 PM	04:14 PM	195	37	157	172	7.1
	09/24/68	918-23-TA-1	06:18 AM	12:20 PM	MEZZAFLINE	918-23-TA-1	06:18 AM	03:23 PM	200	105	273	265	3.9
		918-23-TA-2	12:25 PM	03:23 PM	MEZZAFLINE	918-23-TA-2	06:41 AM	03:47 PM	210	50	312	180	6.8
		918-23-TA-3	06:32 AM	03:27 PM	MIDSOLE	918-23-TA-3	06:41 AM	03:47 PM	210	123	701	155	5.5
		918-23-TA-4	06:50 AM	04:00 PM	WEST	918-23-TA-4	06:40 AM	04:00 PM	200	151	770	184	
		918-23-PAINT	11:07 AM	11:13 AM	WEST	918-23-PAINT-1	11:07 AM	11:21 AM	155	219	10.6	21,030	
		918-24-TA-1	06:54 AM	10:00 AM	MIDSOLE	918-24-TA-1	06:54 AM	10:00 AM	145	30	157	181	
	09/24/68	918-24-TA-2	10:13 AM	11:10 AM	MIDSOLE	918-24-TA-2	10:10 AM	11:10 AM	145	48	136	204	
		918-24-TA-3	11:20 AM	12:20 PM	MIDSOLE	918-24-TA-3	11:20 AM	12:26 PM	145	60	162	370	
		918-24-TA-4	12:41 PM	01:43 PM	MIDSOLE	918-24-TA-4	12:41 PM	01:43 PM	140	43	140	201	
		918-24-TA-5	01:53 PM	04:11 PM	MIDSOLE	918-24-TA-5	01:53 PM	04:11 PM	140	62	220	250	
		918-24-TA-1	06:45 AM	12:37 PM	MEZZAFLINE	918-24-TA-1	06:45 AM	03:30 PM	200	90	300	254	6
		918-24-TA-2	01:01 PM	03:41 PM	MEZZAFLINE	918-24-TA-2	06:55 AM	04:00 PM	200	61	245	240	3.5
	09/24/68	918-24-TA-3	04:55 AM	03:50 PM	MIDSOLE	918-24-TA-3	06:55 AM	04:00 PM	200	152	772	197	
		918-24-TA-4	06:00 AM	04:21 PM	WEST	918-24-TA-4	06:00 AM	04:21 PM	200	231	794	201	
	09/24/68	918-24-OVER-1	03:48 PM	06:16 AM	MEZZAFLINE				101	1405	64		
		918-24-OVER-2	04:15 PM	06:16 AM	MIDSOLE				125	1770	70		

CH = Time Resolved Sample (1 hr average)  
TA = Time Averaged Sample (1 hr, 4, 8, or 16 hr average)

TR = Time Resolved Sample (in hourly)  
TA = Time Averaged Sample (in 4, 8, or 16 hr average)

Table 1. Particulate, Vapor, and Gaseous Hydrocarbon Sampling Data  
Fort Carson, Colorado, September 23 - October 1, 1966  
(Cont.)

MOTOR POOL	DATE	PARTICULATES				VAPORS				SAMPLING VOLUME, ml	PARTICLES, mg/filter	PART. MATTER CONC., $\mu\text{g}/\text{ml}$	TOTAL C1-C6 HC, ppm
		SAMPLE NUMBER	SAMPLING PERIOD		SAMPLING LOCATION	SAMPLE NUMBER	SAMPLING PERIOD		FLAME RATE, ml/min				
			START	STOP			START	STOP					
DISCON	09/25/66	D19-23-TA-1	00:22 AM	04:06 PM	MEZZANTINE	D19-23-TA-1	00:22 AM	04:06 PM	200	84	100		
		D19-23-TA-2	00:40 AM	04:23 PM	MIDDLE	D19-23-TA-2	00:40 AM	04:23 PM	205	127	146		
		D19-23-TA-3	11:51 AM	04:20 PM	WEST					322	310		
		D19-23-TA-OVER-1	04:15 PM	09:22 AM	MEZZANTINE					1715	30		
		D19-23-TA-OVER-2	04:20 PM	09:20 AM	MIDDLE					1913	16		
	09/26/66	D19-26-TA-1	00:24 AM	03:00 PM	MEZZANTINE					85	107		
		D19-26-TA-2	00:24 AM	03:11 PM	MIDDLE	D19-26-TA-1	00:24 AM	03:11 PM	205	79	127		
		D19-26-TA-3	00:44 AM	03:10 PM	WEST					806	195		
		DOL-OUTSIDE INDOOR	00:25 AM	03:44 PM	OUTSIDE	DOL-OUTSIDE INDOOR	00:41 AM	03:42 PM	400	40	40		
		DOL-23-TA-OVER-1	03:23 PM	06:40 AM	LOWER LEVEL					1003	34		
DOL	09/25/66	DOL-23-TA-OVER-2	03:20 PM	06:41 AM	UPPER LEVEL					20	15		
		DOL-23-TA-1	06:43 AM	12:45 PM	TOP STORAGE	DOL-23-TA-1	06:54 AM	03:20 PM	205	55	38		
		DOL-23-TA-2	12:47 PM	03:20 PM	UPPER LEVEL	DOL-23-TA-2	06:50 AM	03:21 PM	307	34	34		
		DOL-23-TA-3	06:53 AM	03:21 PM	LOWER LEVEL					1000	110		
		DOL-26-TA-1	00:44 AM	03:40 PM	UPPER LEVEL	DOL-26-TA-1	00:40 AM	03:40 PM	300	21	21		
		DOL-26-TA-2	00:46 AM	04:00 PM	LOWER LEVEL	DOL-26-TA-2	10:15 AM	04:04 PM	305	124	146		

TR = Time Resolved Sample (ca hourly)  
TA = Time Averaged Sample (ca 4, 8, or 16 hr average)

Table 2. Particulates, Vapor, and Gaseous Hydrocarbon Sampling Data  
Fort Carson, Colorado, September 23 - October 1, 1966  
(Cont'd)

STATION NO.	DATE	PARTICULATES				VAPORS				PARTICLES, mg/dry wt	SAMPLING VOLUME, m3	PART. MATTER CONC., mg/m3	TOTAL C1-C6 HC, ppm
		SAMPLE NUMBER	SAMPLING PERIOD		SAMPLING LOCATION	SAMPLE NUMBER	SAMPLING PERIOD		FLAM MATR., mL/min				
			START	STOP			START	STOP					
478 EXCH	09/29/66	EXP-20-TA-OVER-1	04:25 PM	04:51 AM	WEST TRACK						2670	21	
		EXP-20-TA-OVER-2	04:51 PM	04:55 AM	WEST TRACK						1740	26	
09/30/66		EXP-20-TA-1	00:20 AM	10:05 AM	WEST TRACK	EXP-20-TA-1	00:00 AM	10:05 AM	140		100	07	
		EXP-20-TA-2	10:00 AM	11:00 AM	WEST TRACK	EXP-20-TA-2	10:11 AM	11:00 AM	100		100	01	
		EXP-20-TA-3	11:10 AM	12:17 PM	WEST TRACK	EXP-20-TA-3	11:10 AM	12:14 PM	100		141	01	
		EXP-20-TA-4	12:10 PM	01:10 PM	WEST TRACK	EXP-20-TA-4	12:20 PM	01:10 PM	100		102	37	
		EXP-20-TA-5	01:23 PM	02:00 PM	WEST TRACK	EXP-20-TA-5	01:20 PM	02:00 PM	102		200	25	
		EXP-20-TA-6	00:10 AM	02:35 PM	WEST TRACK	EXP-20-TA-6	00:10 AM	12:10 PM	200		041	15	
		EXP-20-TA-7	00:10 AM	02:35 PM	WEST TRACK	EXP-20-TA-7	00:11 AM	02:35 PM	200		030	12	6.7
		EXP-20-TA-8	00:45 AM	02:00 PM	WEST TRACK	EXP-20-TA-8	00:40 AM	02:00 PM	200		025	26	6.5
		EXP-20-TA-9	00:53 AM	02:34 PM	WEST TRACK	EXP-20-TA-9	00:50 AM	02:34 PM	200		012	10	
10/01/66		EXP-1-TA-1	00:50 AM	10:17 AM	WEST TRACK	EXP-1-TA-1	00:20 AM	10:17 AM	145		51.3	246	
		EXP-1-TA-2	10:30 AM	12:30 PM	WEST TRACK	EXP-1-TA-2	10:20 AM	12:30 PM	140		320	07	
		EXP-1-TA-3	12:51 PM	04:02 PM	WEST TRACK	EXP-1-TA-3	12:51 PM	04:00 PM	130		510	121	
		EXP-1-TA-4	00:00 AM	02:32 PM	WEST TRACK	EXP-1-TA-4	00:20 AM	02:30 PM	205		007	217	
		EXP-1-TA-5	00:07 AM	02:31 PM	WEST TRACK	EXP-1-TA-5	00:20 AM	02:31 PM	200		050	220	6.6
		EXP-1-TA-6	00:54 AM	02:24 PM	WEST TRACK	EXP-1-TA-6	00:20 AM	02:30 PM	200		047	102	6.7
		EXP-1-TA-7	00:50 AM	02:02 PM	WEST TRACK	EXP-1-TA-7	00:20 AM	02:30 PM	200		073	155	

TR = Time Received Sample (to hourly)

TA = Time Averaged Sample (to 4, 8, or 16 hr average)

## Sampling Equipment and Procedures

Sampling systems are described in detail below.

### I. Vapor Phase Sampling

#### A. Specific Analyzers for Carbon Monoxide (CO)

Two continuous monitoring instruments were employed to measure carbon monoxide (CO) levels at the various field locations.

- **Ecolyzer** - The Model 2106 Ecolyzer (National Draeger, Inc., Pittsburgh, PA) is a self-contained unit with sampling pump, flow indicator, meter readout, analog voltage output for recording and providing dual ranges of 0-50 and 0-100 ppm CO full scale. The unit may be operated from its internal rechargeable batteries or from 120 vac line power. The measuring element is an electrochemical cell in which CO is electrooxidized to carbon dioxide at a catalytically active controlled potential electrode. The current becomes a proportional measure of CO concentration. The unit is reasonably immune to interfering gases except for ethylene ( $C_2H_4$ ) and high concentrations of hydrogen ( $H_2$ ) and hydrogen sulfide ( $H_2S$ ). Reproducibility of the instrument is basically  $\pm 1\%$  of full scale (f.s.) and response time is 25 seconds for 90% f.s. The instrument as used at Fort Carson on the second trip was calibrated twice daily and/or at the beginning and end of each run at a given location using a bottled gas standard of 60 ppm CO in air. Continuous recording of the CO level at several locations was made by feeding the voltage output of the Ecolyzer to a Linear Instrument Model 156 miniature flat-bed recorder (Linear Instrument Corp., Reno, NV).
- **MSA Indicator** - The MSA Model V MiniCO<sup>TM</sup> Carbon Monoxide Indicator (Mine Safety Applications Co., Pittsburgh, PA) is a small battery operated hand held unit featuring digital readout to the nearest ppm up to a maximum of 2000 ppm. Access to the sensing element is via an opening in the face of the instrument and atmospheric CO diffuses to the sensor through this opening. The instrument uses an electrochemical polarographic cell in which the CO diffuses through a permeable polytetrafluoroethylene (PTFE) membrane on the sensor face. The unit is quite stable and accurate but suffers serious interferences from hydrogen sulfide ( $H_2S$ ), nitrogen dioxide ( $NO_2$ ), nitric oxide (NO), sulphur dioxide ( $SO_2$ ) and a few other pollution related compounds. Where this unit was used for data collection, sampling for major interfering gases was made using chemical indicator (Draeger) tubes in order to insure accurate CO readings. Response time is 30 seconds for 90% of full scale. The unit was calibrated at 60 ppm using a bottled gas standard at the beginning of each series of measurements and/or twice a day as necessary. The unit was used liberally to check wide areas in and around the fixed monitoring sites and to augment the continuous CO measurements provided by the Ecolyzer.

## B. Adsorption Traps for Major Organics & Toxic Compounds

1. Tenax Traps - For long term sampling and collection of volatile constituents, a large trap previously constructed at ORNL for the source sampling of a coal gasifier (12) was employed. It consists of a glass pipe, ca. 17.5 cm long x 2 cm o.d. filled with approximately 3 g of 35-60 mesh Tenax-GC.
2. Combination Traps - The trapping system employed for the time resolved collection of organic vapor phase constituents was a triple sorbent trap developed at ORNL. The trap consists of a stainless steel tube, 20.5 cm long x 0.46 cm i.d., packed with three sorbent materials. Approximately 1.7 mL of 35-60 mesh Tenax-GC (Alltech/Applied Science) is backed with approximately 0.8 mL of 20-40 mesh Carbotrap (Supelco, Inc.), an uncoated carbon molecular sieve, which is, in turn, backed by 0.3 mL of Ambersorb XE-340 (20-60 mesh, Rohm & Haas). After conventional resin cleaning procedures prior to construction, the material is packed in the stainless steel tubes, separated by small plugs of silylated glass wool, and desorbed for several hours at 270°C with helium at a flow of 20 mL per minute. Desorption flow is always in the direction of the Ambersorb being the upstream end, while collection flow is in the reverse direction. In this manner, constituents breaking through the Tenax are retained by the Carbotrap, and so forth.

## C. Gas Collection for Carbon Dioxide (CO<sub>2</sub>) Determination

Collection of representative volumes of gas at various locations for both time averaged and point source determination was made using small sampling pumps (description follows) and Tedlar gas sampling bags. The contents of filled bags were promptly transferred to glass gas sampling bulbs for return to ORNL and analysis for CO<sub>2</sub> determination using GC with a thermal conductivity detector. Gas samples were transferred from the bags to the gas bulbs using a small diaphragm pump to pull a vacuum on the gas bulb while it is connected to the bag.

Bag contents were also measured on-site for CO<sub>2</sub> using Draeger indicator tubes (description follows) as a cross check and/or back up to later GC determinations.

## D. Low Flow Sampling Pumps

Sampling the volatile organic compounds using the 3 gram Tenax traps and the smaller combination resin adsorption traps was carried out using the DuPont Model P-4000 Constant Flow Air Sampling Pumps (E.I. DuPont de Nemours & Co., Inc., Kennett Square, PA). Frequently the discharge of these pumps was connected to a Tedlar gas bag for gas sample collection (See previous discussion on gas collection.).



These personal air sampling pumps feature automatic flow control of  $\pm 5\%$  over a range of 20 cc/minute to 4.0 liters/minute. The units employ a diaphragm actuated by a motor driven eccentric crankshaft to create air flow. Pressure drop resulting from air flow across an internal needle valve is used to modulate a servo amplifier to regulate motor speed and thus affect flow rate in a closed loop control mode. The stated  $\pm 5\%$  control accuracy is valid for an external pressure drop (across the absorption traps) of no more than 25 inches water column (w.c.) up to 2.0 liters/minute and 10 inches w.c. from 2.0 liters/minute to 4.0 liters/minute. Operation at greater pressure drops than these is possible with a sacrifice in control.

The 3 gram Tenax traps offered little flow resistance and sampling rates of ca. 300 mL/min could be automatically maintained by the pumps. The pressure drop through the combination traps exceeded the control limits of the pumps, however, and the pumps were simply operated at maximum capacity for the higher pressure drops involved. Flow rate calibrations of the pumps used for the 3 gram Tenax traps were made periodically to insure the automatically controlled rates were being maintained. Flow rate calibration involving the combination traps was made at the beginning and end of each sample in order to accurately document the total volume involved. Typically, the flow rate through the combination traps was ca. 150 mL/min.

Flow measurements were made using either a thermal mass flowmeter or less frequently, a conventional soap film volumetric standard. The thermal mass flowmeter used was the Kurz Model 581 Pocket Flow Calibrator (Kurz Instruments, Inc., Carmel Valley, CA) with dual ranges of 0-0.5 and 0-5 liters/minute. The manufacturer states an overall accuracy of  $\pm 3\%$  and supplies an NBS traceable calibration certificate. The meter readings were periodically verified at Fort Carson using the soap film flow standard and found to be within the stated accuracy.

#### E. Chemical Indicator Tubes

Commercially available colorimetric chemical indicator tubes were used for spot determinations of carbon monoxide (CO), hydrogen sulfide (H<sub>2</sub>S), sulphur dioxide (SO<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), oxides of nitrogen (NO<sub>x</sub>) and petroleum hydrocarbons. The most sensitive available Draeger tubes (National Draeger, Inc., Pittsburgh, PA) were generally used for each particular gas. The Draeger Model 31 gas detector hand pump was used to draw the required volumetric sample through the tubes as required. The tubes were direct reading in parts per million (ppm) and the manufacturer states relative standard deviations for each tube group. For the tubes used in these tests, the relative standard deviations varied from 5 to 15%.

#### F. Personal Diffusion Dosimeter Tubes

Small diffusion type dosimeter tubes for CO, H<sub>2</sub>S and SO<sub>2</sub> were provided to be worn by ORNL personnel in the work areas surveyed on the second trip. The specific tubes used were Sensidyne (Sensidyne, Inc., Largo, FL) units as follows: Type 1D for CO (50-1000 ppm·hr), Type 5D for SO<sub>2</sub>.

(2-100 ppm·hr) and Type 4D for H<sub>2</sub>S (10-200 ppm·hr). As can be seen from these time integrated ranges, the tubes are not particularly sensitive to low concentration levels. They are, however, useful in detecting unexpected "hot spots" or pockets of high toxic gas concentrations accidentally encountered by a worker.

## II. Particulate Phase Sampling Apparatus

### A. High Volume Sampling

#### 1. Filters

Filters for both integrated exposure sampling and time-resolved exposure sampling were polytetrafluoroethylene (PTFE) coated glass sub-micron fiber type. The material is commercially available as Pallflex Fiberfilm Type T60A20 (Pallflex Corp., Putnam, CT). Both 8"x10" rectangular filters and 4" diameter filters were used in appropriate holders as dictated by the volume requirements of the particular measurement. On the second trip, all filter samples were weighed on-site immediately before and promptly after sampling to allow the total suspended particulate matter concentration to be calculated. A Sartorius Model 1205 Electronic Laboratory Balance (Sartorius GmbH, Goettingen, West Germany) was used to determine filter weight changes.

After post exposure weighing, each filter was carefully folded and wrapped in pre-cleaned aluminum foil for transport to ORNL for analysis.

#### 2. Sampling Pumps

Two basic pump types were used for all high volume sampling. Either of the units could be fitted with an 8"x10" filter holder or a 4" (normal) filter holder as required by the experimental design.

##### a. ORNL Hi-Vol Sampling Pump

Two ORNL designed high volume pumps were used where the highest sampling volumes were needed. Flow rates up to about 2400 liters/minute were possible using the 8"x10" Pallflex filter. Each pump consisted of a basic Ametek-Lamb Electric Vacuum Motor Model I.S. 14586 (Lamb Electric Division, AMETEK Corp., Kent, OH) which is essentially a two-stage motor driven turbine unit designed for hazardous service (explosive proof). An explosion proof housing was fabricated at ORNL which included the industry standard 4" screwed inlet for large filter holders and also suitable stable support legs for field use.

Filter holders used with these pumps included the Staplex Model SH4 (Staplex Company, Air Sampler Division, Brooklyn, NY) for 4" round filters and the Model SH810 for 8"x10" filters.

An ORNL designed extension system was fabricated in order to permit sampling inaccessible or hard-to-reach areas such as the Building 8000 roof exhaust for dynamometer engine tests, the elevated exhaust of vehicles such as the 5 ton truck, ammunition hauler (GOER), etc. This extension consisted of four-foot sections of 4" diameter stainless steel flexible tubing combined with sections of rigid tubing. An adapter was fabricated of stainless steel to couple these inlet sections to the upstream side of an 8"x10" filter holder. The tubing is quickly joined in the field to provide the desired length, up to about twelve feet maximum.

#### b. Staplex Sampling Pump

Four Staplex Model TFIA Air Sampling pumps were employed extensively for "medium" high volume particulate sampling using both the 8"x10" and the 4" filter holders and filters. Maximum flow rates in the vicinity of 1800 liters/minute were possible using these units with the 8"x10" filters.

#### c. Calibration

One of the problems associated with either of the sampling pumps described (as well as all commercially available high volume units) is their flow rate dependence on line voltage as well as, to a lesser extent, to filter loading. Filter loading was not considered to be a major problem in the Fort Carson studies, but line voltage fluctuations were seen as somewhat more serious. Coupled with unknown line voltages at each particular sampling location at Fort Carson was the voltage drop associated with extension cord lengths in excess of two hundred feet in some cases.

Accordingly, it was decided to calibrate each pump, with a blank filter in place, and carefully plot line voltage versus flow rate. Each sampling pump was connected to a variable voltage source (autotransformer) and the voltage varied from 90 volts to 120 volts while the flow rate was carefully measured. The inlet of each filter holder used was fitted with a temporary straight tubing section (ca., 4" diameter) approximately four feet long such that an anemometer traverse could be made to provide a velocity profile for flow rate calculation. An Alnor Type 8500 Thermo-Anemometer (Alnor Instrument Co., Niles, IL) was used for this purpose after it had been calibrated against an NBS traceable standard. Measurements were also made on the inlet of the filter holders without the inlet tube and similar flow figures were

obtained by careful traverse measurements. Three digital voltameters were used to measure voltages at Fort Carson. Each of these meters was calibrated against an a.c. voltage standard by the ORNL Electrical Standards Laboratory prior to these tests and their use at Fort Carson. During all tests at Fort Carson, the voltage at the high volume sampling pumps was noted before and after each sampling run and used to calculate the volume.

#### B. Low Volume Particulate Filter Collection

The inlet of each of the aforementioned Tenax or combination traps was preceded by a filter to prevent particulate matter from contacting the trap media. In many cases, a 47 mm diameter Pallflex Type T60A20 filter was used in a BGI Type F7 metal holder (BEI Inc., Waltham, MA). The filters were preserved after use as a possible reference or back up to high volume particulate sampling. In cases (predominantly on the first trip) where specific collection of small quantities of particulates were to be collected for metals analysis, 47 mm diameter Teflon membrane filters (Millipore Type FH, 0.5 micron) were substituted.

#### C. Particle Size Distribution Using a Cascade Impactor

A small low volume cascade impactor (IN-TOX Type 02-100 Mercer Impactor, IN-TOX Products, Albuquerque, NM) was employed to provide an approximate size distribution of collected particulate matter at various locations. Collection on glass substrates was used and relative density ratios were estimated by optical comparison to determine size relationships.

The flow rate required for this particular impactor was 1.0 liter/minute and this flow rate was maintained in the field by using an ORNL designed sampler. In this sampler a Neptune 4K diaphragm pump (Neptune Products, Inc., Dover, NJ) is used as a vacuum source and a Moore Model 63BD flow controller (Moore Products, Co., Spring House, PA) is employed to maintain a constant flow rate as set on the panel mounted needle valve and rotameter. Flow control within  $\pm 2\%$  is routinely obtained.

## ORGANIC CHEMICAL COMPOSITION OF DIESEL ENGINE EXHAUST AND COMPARISON WITH THE MOTOR POOL WORKPLACE ATMOSPHERE

As described in the previous section, the first sampling trip to Fort Carson, CO focused mainly upon the collection of exhaust samples from diesel engines mounted in vehicles and in dynamometer test stands, and to a lesser extent, workplace atmosphere samples from two motor pool garages. This section presents the results of the characterization of those samples.

### Composition of Diesel Engine Exhaust

The gross characteristics of total suspended particulate matter (TSP) concentration, carbon dioxide concentration, and particle size distribution are listed in Table 3 for the samples collected from diesel engine exhaust and workplace atmospheres in the September, 1984, sampling trip to Fort Carson. The filters used in the first sampling trip could not be accurately weighed in the field. Hence, the unloaded filter weights were estimated at ORNL from the average weight of three unsampled filters remaining from the same lot. The standard deviation of those three weights was 40 mg, and this uncertainty in the initial filter weights must be considered in conjunction with the estimated TSP. The TSP concentrations ranged from ca. 1.7 to 12 mg/m<sup>3</sup>. The TSP in undiluted exhaust from a 5.7 L experimental diesel engine under Federal Test Procedure conditions is reported (13) to be 85 mg/m<sup>3</sup>, which suggests a ca. 10-fold dilution of the exhaust collected at Fort Carson. The range of TSP values is a result not only of the different engine sizes and operating conditions, but also the different dilutions of the raw exhaust. The carbon dioxide concentrations determined by gas chromatography (GC) ranged from 0.18 to 3 vol%, and also are affected by engine operation conditions and exhaust dilution. The carbon dioxide concentrations determined for the APC exhaust do not appear to track the TSP concentrations, perhaps from different engine operating conditions. The most concentrated exhaust was the sample no. 21-D-1 collected from the dynamometer test stand exhaust stack when an M-60 tank engine was being tested over an RPM range of 750 to 2,400 (see Appendix Table A-6). In spite of the different sampling and engine operating conditions, the particle size distributions were quite similar. The mass median aerodynamic particle size ranged from 0.2 to 0.5  $\mu$ m, with geometric standard deviations of 2 to 6. These very finely sized particles are in line with the results of other studies (14) of diluted raw exhaust. Thus, the diesel engine exhaust was found to consist of a fairly concentrated aerosol of respirable, sub- $\mu$ m particles.

The gas chromatographable major organic composition of the particulate phase organics collected by filtration was determined by ultrasonic extraction of the filters in toluene after spiking with an internal standard (IS), volume reduction of the solvent, and capillary column GC. An HP-5880 gas chromatograph equipped with a fused silica column of 30 m x 0.25 mm ID x 0.25  $\mu$ m film of bonded DB-5, a Level IV data

Table 3. Summary of Total Particulate Matter, Carbon Dioxide, and Particle Size Distribution Measurements of Diesel Engine Exhaust and Area Samples

Filter No.	Sample Type	Estimated TSP <sup>a</sup> , mg/Filter	TSP Concentration, mg/m <sup>3</sup>	CO <sub>2</sub> Concentration,		Particle Size Distribution, $\mu$ m	GSD <sup>e</sup>
				Vol. %	GC <sup>c</sup>		
21-D-1	M-60-Dynamometer	950	12	3.3	3.0		
24-D-1	M-60-Dynamometer	530	5.8		0.42	0.4	4
21-D-2	APC-Dynamometer	290	2.4	0.6		0.4	4
24-D-2	APC-Dynamometer	410	3.7		0.18		
25-A-1	M-60	260	2.8	0.24	0.28	0.5	4
24-E-2	M813	250	2.6	0.57	0.68	0.5	5
24-E-3	Truck	270	3.7	0.62		0.3	3
24-E-4	Tank Ret.	170	1.8		0.22	0.3	2
24-E-5	Blazer	120	1.7	0.42	0.30	0.2	2
25-E-2	Dozer	630	6.7	0.80	0.93	0.2	6
25-E-1	APC	860	9.1	0.41	0.32	0.4	3
26-A-2	Truck	350	3.7	0.18	0.23	0.4	4
26-A-3	GOER	460	4.9	0.81	0.97	0.4	3
24-Area E-1	EMP	350	0.44				
25-Area E-3	EMP	200	0.23				
25-Area D-1	Bkgd	140	0.3				
25-Area A-1	AMP	25	0.04				
26-Area D-1	Bkgd	70	0.13				
26-Area A-1	AMP	170	0.22				

<sup>a</sup>TSP = total suspended particulate matter collected by the filter. ( $\pm 40$  mg)

<sup>b</sup>CO<sub>2</sub> concentration estimated on-site by colorimetric detector tube.

<sup>c</sup>CO<sub>2</sub> concentration estimated at ORNL by GC analysis of gas bulb sample.

<sup>d</sup>MMAD = mass median aerodynamic diameter.

<sup>e</sup>GSD = geometric standard deviation.

system, splitless injector, and flame ionization detector was used for all particulate extract analyses. The column was temperature programmed from 80°C (5 min isothermal hold) to 200°C at 3.5°C/min, and then to 280°C at 2.8°C/min with a hydrogen carrier gas flow rate of 1.3 mL/min. A hydrogen leak detector shut off the instrument power if hydrogen was detected in the chromatograph oven. The injector temperature was 270°C and the detector temperature was 290°C. Sample aliquots of 2 µL were injected using the solvent flush technique. The limit of detection was ca. 0.1 mg/g in the TSP, and precision was estimated at  $\pm 10\%$  RSD. Accuracy was difficult to define without standard reference materials, but probably was within  $\pm 10\%$ . Figure 5 shows the chromatogram for sample 25-A-1, which was collected from the exhaust of an M-60 tank. The numbered major peaks are identified in Table 4, and approximate concentrations are calculated as mg/g of particulate matter and µg/m<sup>3</sup> of diluted exhaust. The major components were a series of n-alkanes ranging from C<sub>15</sub> through at least C<sub>30</sub> at concentrations from <0.1 to 7.4 mg/g. In addition, pristane, phytane, and numerous alkylated 2- and 3-ring polycyclic aromatic hydrocarbons (PAH) were found at much lower levels relative to the n-alkanes. All of these compounds have been confirmed in diesel engine exhaust (15), and there is evidence (16) that the hydrocarbon distribution extends to at least C<sub>40</sub>. Tentative identifications of fluorenone, dibenzothiophene, and two methyl dibenzothiophenes also were made, but the latter two are difficult to distinguish from C<sub>4</sub>- and C<sub>5</sub>-naphthalenes (respectively) by mass spectra alone. The sum of these identified species totaled 6.8 wt% of the particulates. Additional organic matter was present but was not readily identifiable. This was indicated in the remaining peaks and also in the baseline rise in the chromatogram. The latter, which was not found in the blanks, probably was contributed by polar compounds which do not chromatograph well, and by the pileup of numerous trace-level constituents.

These chromatograms of the major organic compounds in the crude particulate extracts are highly useful for comparing the particulate organic composition of exhaust from different vehicles and also sources contributing to the organic matter in the exhaust. Figure 6 compares two potential sources of organic compounds to the diesel engine exhaust. The chromatogram at the top of the figure is almost identical in its major organic compounds to those of the GOER engine exhaust. The former was generated by pipetting a few µL of DF-2 onto a filter pad and drawing air through the filter at the same linear velocity and duration as for the exhaust sampling. The filter was then extracted and analyzed as were the exhaust particulate filters. Comparison of the chromatograms strongly suggests that unburned fuel (5,13,15,16) contributes much of the chromatographable major organic compounds found in the exhaust particulate matter. The baseline rise, or "hump", appears associated with higher molecular weight material, such as the crankcase oil from the GOER engine, shown at the bottom of the figure. Gel permeation chromatography studies (13) of the molecular weight distributions of exhaust particulates and crankcase oil support this contention. Although some of this matter may arise from leaking piston oil rings, some also may be contributed by the combustion process itself. Additionally, the chromatograms show indications of fuel

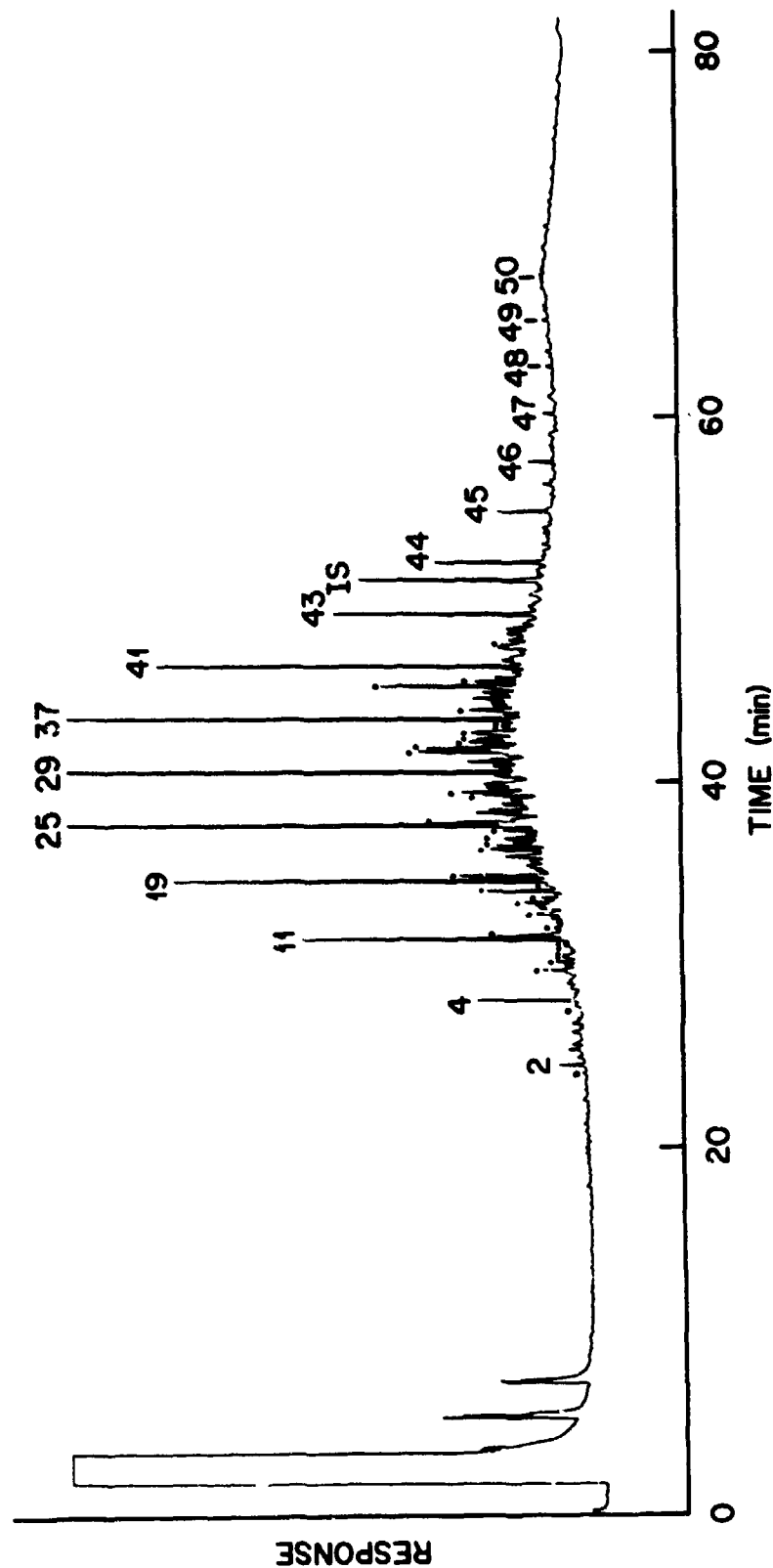


Figure 5. Capillary Gas Chromatogram of the Chromatographable Major Organic Particulate Phase Compounds in the Exhaust of an M-60 Tank (See Table 4 for compound identification and quantification. 30 m DB-5 column temperature programmed from 80° [5 min isothermal hold] to 200°C at 3.5°/min, and to 280°C at 2.8°/min.)



Table 4

Semiquantitative Determination of Major Particulate Phase Organic Compounds in Exhaust  
of M-60 Tank (Sample 25-A-1)

Peak No. <sup>a</sup>	Identification <sup>b</sup>	Concentration <sup>c</sup>	
		mg/g	µg/m <sup>3</sup>
1	C <sub>3</sub> -Naphthalene	< 0.1	< 0.3
2	n-C <sub>15</sub> H <sub>32</sub>	0.17	0.48
3	Fluorene	< 0.1	< 0.3
4	n-C <sub>16</sub> H <sub>34</sub>	1.0	2.8
5	Hydrocarbon	0.2	0.56
6	Hydrocarbon (Maybe 2-Methyl C <sub>15</sub> )	0.2	0.56
7	Hydrocarbon	0.1	0.3
8	Hydrocarbon	0.1	0.3
9	C <sub>2</sub> -Acenaphthalene/C <sub>1</sub> -Fluorene	< 0.1	< 0.3
10	C <sub>2</sub> -Acenaphthalene/C <sub>1</sub> -Fluorene	< 0.1	< 0.3
11	n-C <sub>17</sub> H <sub>36</sub>	5.3	15
12	Pristane	1.2	3.4
13	Fluorenone	< 0.1	< 0.3
14	Dibenzothiophene (C <sub>4</sub> -Naphthalene?)	0.5	1
15	Hydrocarbon	0.2	0.6
16	Hydrocarbon (Maybe 3-Methyl C <sub>17</sub> )	0.1	0.3
17	Phenanthrene	1.5	4.2
18	Anthracene + Hydrocarbon	< 0.1	< 0.3
19	n-C <sub>18</sub> H <sub>38</sub>	4.5	13
20	Phytane	1.0	2.8
21	C <sub>1</sub> -Dibenzothiophene (C <sub>5</sub> -Naphthalene?)	1	3
22	Hydrocarbon	0.4	1
23	C <sub>1</sub> -Dibenzothiophene (C <sub>5</sub> -Naphthalene?)	0.7	2
24	C <sub>1</sub> -Phenanthrene	0.7	2
25	n-C <sub>19</sub> H <sub>40</sub>	6.9	19
26	2-Methyl Phenanthrene	2.2	6.2
27	C <sub>8</sub> -Naphthalene	0.7	2
28	Hydrocarbon	0.7	2
29	n-C <sub>20</sub> H <sub>42</sub>	7.4	21
30	C <sub>2</sub> -Phenanthrene	2	6
31	C <sub>2</sub> -Phenanthrene	2	6
32	C <sub>2</sub> -Phenanthrene	0.9	3
33	Fluoranthene	0.6	2
34	C <sub>7</sub> -Naphthalene	0.9	6
35	Hydrocarbon	0.3	0.8
36	C <sub>2</sub> -Phenanthrene	0.3	0.8
37	n-C <sub>21</sub> H <sub>44</sub>	7.0	20
38	Pyrene	1.1	3.1
39	C <sub>3</sub> -Phenanthrene	3	8
40	C <sub>3</sub> -Phenanthrene	1	3
41	n-C <sub>22</sub> H <sub>46</sub>	4.9	14
42	Benzo(b)fluorene	0.5	1
43	n-C <sub>23</sub> H <sub>48</sub>	3.1	8.7
44	n-C <sub>24</sub> H <sub>50</sub>	1.5	4.2
45	n-C <sub>25</sub> H <sub>52</sub>	1.0	2.8
46	n-C <sub>26</sub> H <sub>54</sub>	0.35	0.98
47	n-C <sub>27</sub> H <sub>56</sub>	0.15	0.42
48	n-C <sub>28</sub> H <sub>58</sub>	< 0.1	< 0.3
49	n-C <sub>29</sub> H <sub>60</sub>	< 0.1	< 0.3
50	n-C <sub>30</sub> H <sub>62</sub>	< 0.1	< 0.3

<sup>a</sup>See Figure 5.

<sup>b</sup>Generic identifications are tentative and other isomers are possible.

<sup>c</sup>Concentration estimates should be considered semiquantitative because of incomplete resolution and baseline rise. However, data for n-paraffins should be more accurate ( $\pm 10-20\%$ ) because of their higher relative concentrations. Units are mg per g of particulate matter and µg per m<sup>3</sup> of diluted exhaust.

components in the crankcase oil, as would occur from leaking piston oil rings. These results suggest that the diesel engine exhaust particulate organic component of the workplace atmosphere consists of combustion products and unburned fuel and crankcase oil.

Comparison of Figures 5-7 shows that the major organic particulate compounds in the exhausts of the M-60 tank, the M-60 tank engine mounted in a dynamometer, and a GOER are highly similar qualitatively. They all share the same major compounds. This is expected because they all were diesel engines and all were operating on diesel fuel at Fort Carson. Differences in the running cycles in addition to engine condition were the main variations between samples collected from the M-60 engines mounted in the vehicles versus the dynamometers. The APC had a different engine. The main differences in the particulate organics were quantitative. The distribution of the baseline rise in the chromatograms and the absolute amounts of the various components varied. Table 5 compares quantitative measurements of four major organic compounds, calculated as mg/g in the TSP and  $\mu\text{g}/\text{m}^3$  in the exhaust. It is evident that the dynamometer samples do not reproduce well calculated either as particulate or air concentrations. The vehicle samples are much more concentrated than the dynamometer samples for the APC, and less so for the M-60 tank. These results show that the different diesel engines present in a motor pool garage can contribute the same organic compounds, but in different amounts and ratios to the workplace atmosphere.

Two highly tumorigenic and mutagenic constituents, benzo[a]pyrene (BaP) and 1-nitropyrene (1-NPy), were isolated from two of the exhaust particulate extracts by semipreparative scale, normal phase high performance liquid chromatography, and were measured using capillary column GC-mass spectrometry with selected ion monitoring and the method of internal standards (17). The results for two particulate samples collected from the exhaust of an M-60 tank and an M-60 tank engine mounted in a dynamometer test stand are listed in Table 6 in comparison with data taken from the literature. For these much more toxic components, the concentrations are in the low  $\mu\text{g}/\text{g}$  and  $\text{ng}/\text{m}^3$  concentration ranges. The results are consistent with the literature, because of the considerable variability which could be attributed to such factors as engine size, fuel, condition, and running cycle as well as sampling and analytical variability. A recent study reported (28) an order of magnitude differences in the particulate concentrations of BaP and 1-NPy from automotive engines as a function of fuel composition and injection timing. As for the major organic compounds, the vehicle sample was more concentrated than the dynamometer sample.

The vapor phase organic compounds from diesel engine exhaust were determined as a contributor to the workplace atmosphere. The organic compounds collected in Tenax traps were determined by thermal desorption capillary column GC (29). A portion of the homogenized Tenax unloaded from a trap was thermally desorbed at  $250^\circ\text{C}$  for 30 minutes in a 1.5 mL/min flow of helium, and the compounds liberated were cryogenically focused at the head of the capillary column before

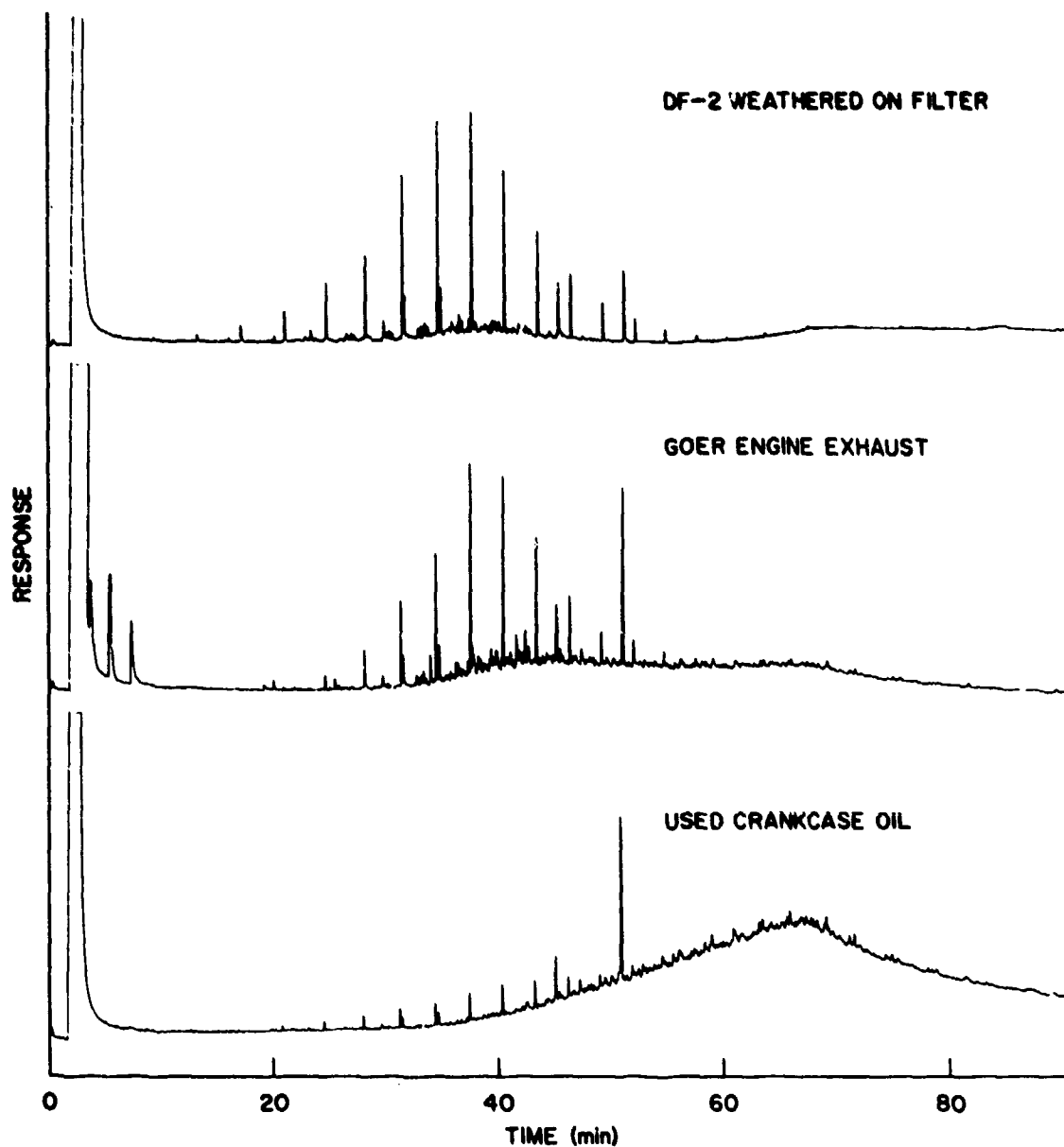


Figure 6. Comparison of Major Chromatographable Organic Compounds in GOER Engine Exhaust, DF-2 Weathered on a Filter, and GOER Crankcase Oil (For GC conditions, see Figure 5)

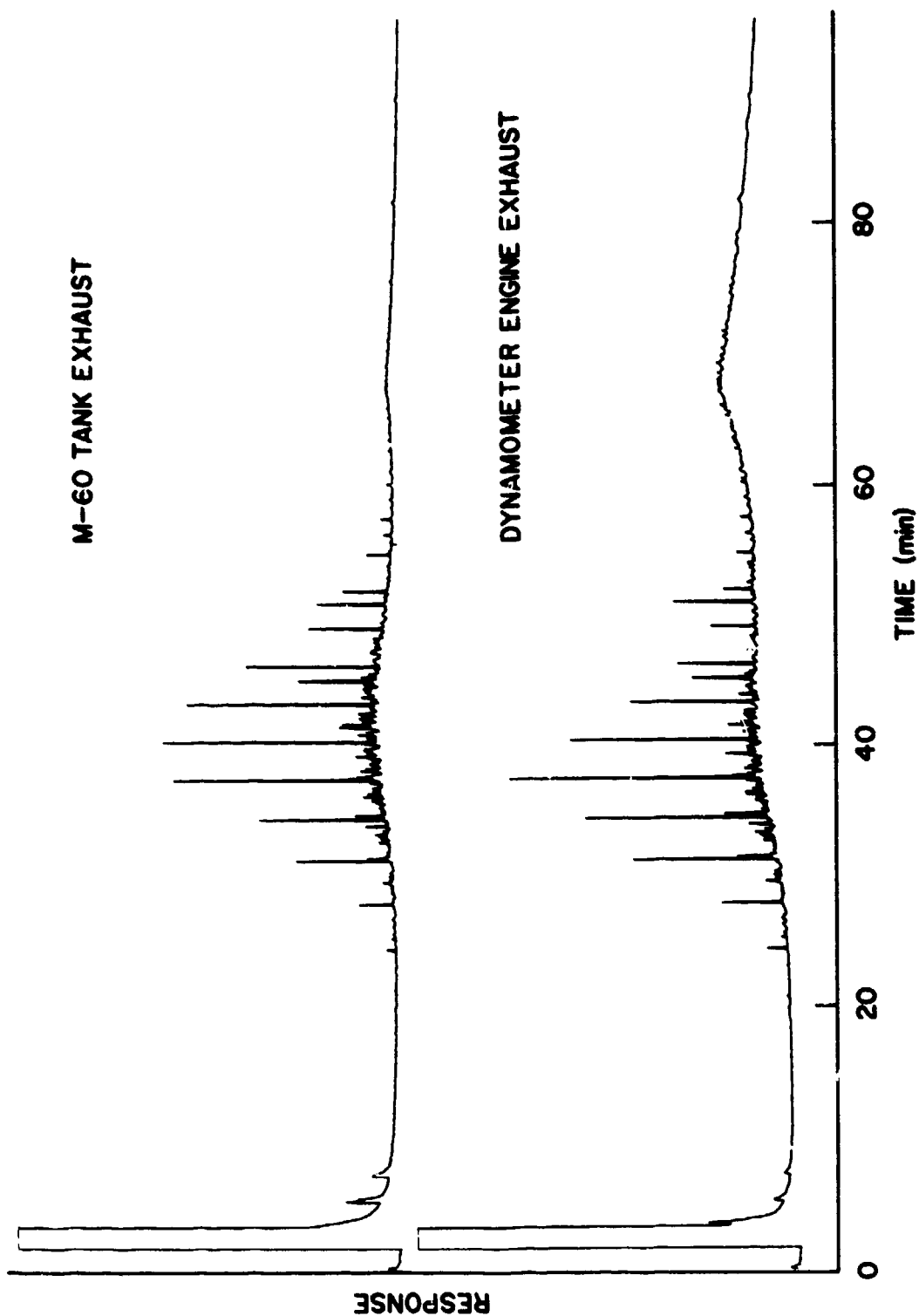


Figure 7. Comparison of the Major Chromatographable Organic Particulate Phase Organic Compounds in M-60 Engine Exhaust from a Vehicle and a Dynamometer Test Stand (For GC conditions, see Figure 5)

Table 5. Comparison of Particulate Organic Indicator Compounds  
in the Exhausts of M-60 Tank and APC Engines Mounted in the  
Vehicles and Dynamometers

Concentration in TSP, mg/g			
<u>Constituent</u>	<u>M-60 Tank</u>		
	<u>Vehicle</u> <u>25 A-1</u>	<u>Dyna.</u> <u>24 D-1</u>	<u>Dyna.</u> <u>21 D-1</u>
C <sub>17</sub>	5.3	3.2	5.5
C <sub>18</sub>	4.5	2.6	4.5
C <sub>19</sub>	6.9	3.2	3.6
C <sub>20</sub>	7.4	2.6	2.4
<u>Constituent</u>	<u>APC</u>		
	<u>Vehicle</u> <u>25 E-1</u>	<u>Dyna.</u> <u>24 D-2</u>	<u>Dyna.</u> <u>21 D-2</u>
C <sub>17</sub>	10.8	0.4	1.8
C <sub>18</sub>	5.9	0.5	2.2
C <sub>19</sub>	5.5	1.1	2.4
C <sub>20</sub>	3.9	1.0	1.8
Air Concentration, $\mu\text{g}/\text{m}^3$			
<u>Constituent</u>	<u>M-60 Tank</u>		
	<u>Vehicle</u> <u>25 A-1</u>	<u>Dyna.</u> <u>24 D-1</u>	<u>Dyna.</u> <u>21 D-1</u>
C <sub>17</sub>	15	18	6.9
C <sub>18</sub>	13	15	5.7
C <sub>19</sub>	19	18	4.5
C <sub>20</sub>	21	15	3.0
<u>Constituent</u>	<u>APC</u>		
	<u>Vehicle</u> <u>25 E-1</u>	<u>Dyna.</u> <u>24 D-2</u>	<u>Dyna.</u> <u>21 D-2</u>
C <sub>17</sub>	99	0.7	0.4
C <sub>18</sub>	54	2.2	0.5
C <sub>19</sub>	51	4.1	0.6
C <sub>20</sub>	35	3.8	0.4

Table 6. Comparison of Benzo(a)Pyrene and 1-Nitropyrene Determinations with Literature Data

Filter Sample	Description	Benzo(a)pyrene			1-Nitropyrene		
		µg/s TSP	ng/m <sup>3</sup> /ppm CO <sub>2</sub>	ng/m <sup>3</sup>	µg/s TSP	ng/m <sup>3</sup> /ppm CO <sub>2</sub>	ng/m <sup>3</sup>
24-D-1	M-60, Dyn	11	$1.5 \times 10^{-2}$	63	0.32	$4.3 \times 10^{-4}$	1.8
25-A-1	M-60, Vehicle	17	$1.7 \times 10^{-2}$	48	2.1	$2.0 \times 10^{-3}$	5.7
----- Literature -----							
Ref. 16	5.7 L GM Diesel	2.2	-	-	8.0	-	-
Ref. 13	5.7 L Expl. Diesel	5.1	-	430	-	-	-
Ref. 13	-	32	-	-	-	-	-
Ref. 19	(CBC CAPE)	0.3 to 23	-	-	-	-	-
Ref. 20	Hv Duty Diesel	-	-	-	0.13 to 14	-	-
Ref. 21	Cummins VTB-903	-	-	-	0.45	-	-
	IH DT-466	-	-	-	6.4	-	-
	Volvo TD-100C	-	-	-	6.8	-	-
	Cat. 3046 DITA	-	-	-	14.7	-	-
Ref. 22	GM Diesel Cars	5.1 to 9.2	-	130 to 230	7.9 to 8.5	-	140 to 180
Ref. 23	-	-	-	-	7	-	-
Ref. 24	-	-	-	-	8.6	-	-
Ref. 25	Automobile	-	-	-	10	-	-
Ref. 26	VW	-	-	-	16 to 103	-	-
Ref. 27	VW	25 to 62	-	-	-	-	-

the column oven was temperature programmed. A Perkin-Elmer Sigma II gas chromatograph equipped with a fused silica capillary column, 60 m x 0.32 mm ID x 1.0  $\mu$ m film DB-1 bonded phase, a flame ionization detector, and an HP-3390 reporting integrator were used with this set of sorbent trap samples. The column oven was temperature programmed from ambient (ca. 25°C held isothermally for 10 min) to 250°C at 2°C/min and held at 250°C for 60 min. The helium carrier gas flow rate was 1.5 mL/min. External standards applied to a sorbent trap and analyzed in the same manner as the samples were used for calibration. The absolute sensitivity of the analysis was in the range of ca. 1 to 10 ng per compound. Reproducibility was ca.  $\pm$  10 to 20% RSD, and accuracy was expected to be in a similar range. The vapor phase organic compounds collected from the exhaust of an M-60 tank engine mounted in a vehicle and in a dynamometer test stand are shown at the bottom of Figure 8. The compounds range from the C<sub>6</sub> through at least the C<sub>18</sub> n-alkanes and include benzene and a series of alkyl benzenes (30-32). The observation of some overlap in composition with the more volatile compounds in the particulate phase (compare with Table 3) confirms earlier work (16). This overlap is probably a result of the vapor-particle partitioning of these compounds as well as their sublimation from the filter during the sample collection. Quantitative determinations of these compounds are listed in Table 7. As is evident also in the figure, the n-alkanes are the major compounds, although benzene and toluene also are relatively concentrated. The air concentrations of these volatile organic compounds are approximately an order of magnitude higher than those of the particulate organics (Table 4).

Comparing the results for the vapor phase organics from vehicle and dynamometer-mounted M-60 tank engines with those (Table 5) for the particulate phase organics shows similar variability in the distributions of components. The vapor phase organics also were generally more concentrated in the vehicle sample than in the dynamometer sample, as is graphically evident in Figure 8. The differences in composition can be affected by factors such as engine condition, degree of warm-up, speed, and load. These results reinforce the earlier observation that the diesel engine exhaust component of the workplace atmosphere is a highly complex and also variable source.

#### Comparison of the Composition of Diesel Engine Exhaust with the Motor Pool Workplace Atmosphere and the Ambient Outside Background

The question of the similarity of diesel engine exhaust to the motor pool workplace atmosphere and its relevance as a surrogate for the latter in the design of animal toxicology studies can be examined by comparing the analytical results for diesel engine exhaust with those for area sampling conducted at the 4/68th Armored and Fourth Engineering Division motor pools. As regards the physical characteristics of the aerosols, the major gross differences determined were in the TSP (Table 3). As expected, the TSP was at least 10-fold more concentrated in the diluted exhaust (1.7-12 mg/m<sup>3</sup>)

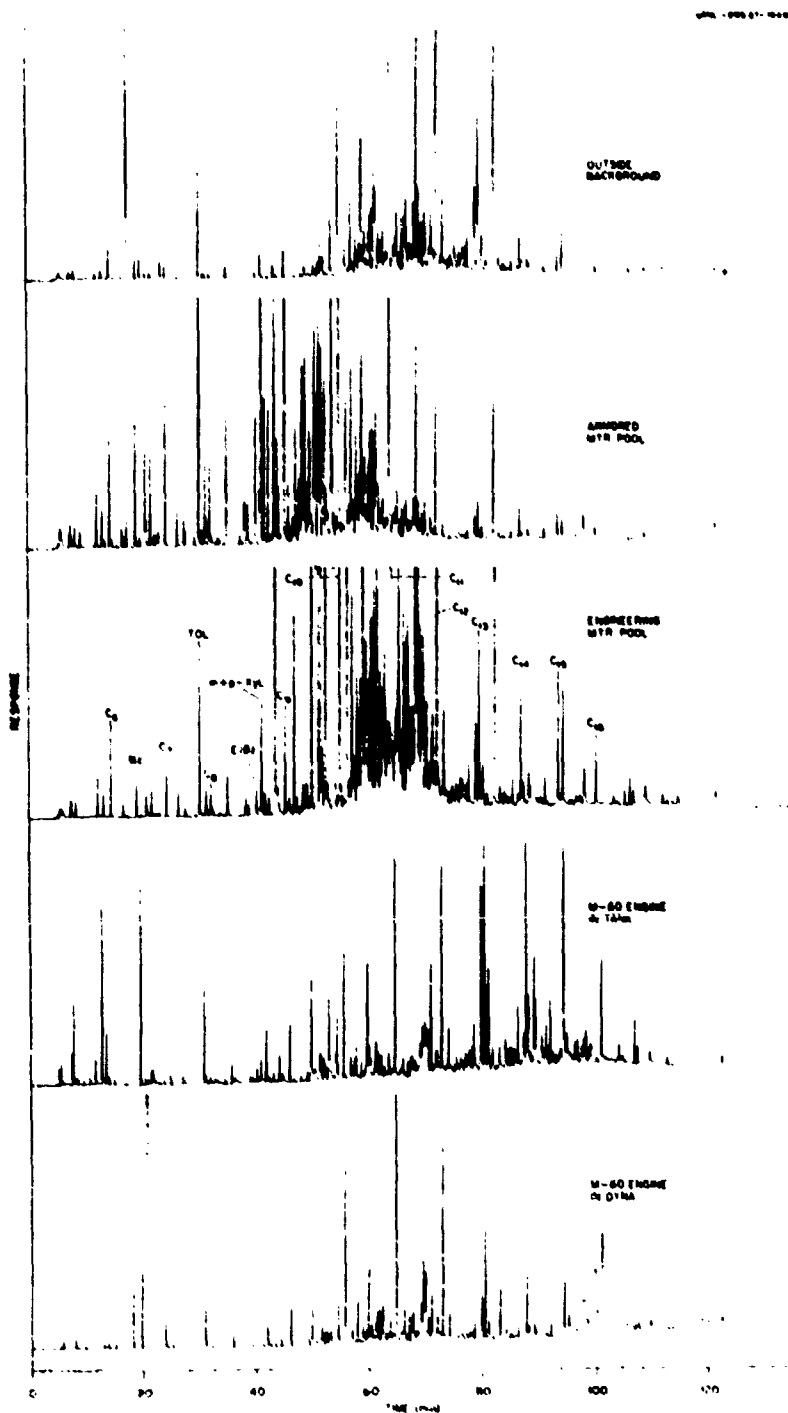


Figure 8. Comparison of the Major Vapor Phase Organic Compounds in Ambient Outside Air (28 L), Workplace Air at the 4/68th Armored Brigade (23 L) and Fourth Engineering Bn (25 L) Motor Pools, and M-60 Tank (0.9 L) and Dynamometer Test Stand Exhaust (1.0 L) (60 m DB-1 capillary column temperature programmed from 25°C [10 min isothermal hold] to 250°C at 2°/min and hold isothermally at 250°C for 60 min)



Table 7. Comparison of Vapor Phase Organic Compounds in Engine Exhaust,  
Motor Pool Workplace Atmospheres, and the Ambient Outside Background in September, 1984

Compound	Concentration, $\mu\text{g}/\text{m}^3$					
	M-60 Tank Engine		4/68th Armored Motor Pool		Engineering Motor Pool	
	Dynamometer 24-D-1	Tank 25-A-1	26 Area A-1	25 HVA-A-1	24 E-1	Background 26 TA-A-1
n-Pentane					0.4	1.3
n-Hexane	6.6	9.5	4.2	0.8	2.7	0.9
Benzene	91	220	5.5	1.5	1.4	0.8
n-Heptane	6.3	15	6.0	0.6	1.9	3.9
Toluene	50	120	24	3.3	6.4	0.6
n-Octane	15	29	5.6	0.7	2.8	1.4
Ethyl Benzene	3.5	34	7.1	0.4	1.4	1.7
m-Xylene	27	81	31	1.6	6.4	1.1
n-Nonane	48	69	33	1.3	4.4	10
n-Decane	210	170	43	1.7	27	33
n-Undecane	460	280	30	1.6	86	19
n-Dodecane	230	270	7.0	1.2	27	8.0
n-Tridecane	130	290	2.9	0.8	7.4	2.7
n-Tetradecane	78	290	2.1	0.8	5.6	0.9
n-Pentadecane	81	360	1.5	0.8	4.4	0.4
n-Hexadecane	< 430 <sup>a</sup>	160	0.6	ND	2.6	

<sup>a</sup>Interference prevented accurate measurement.

than in the workplace atmospheres (0.04-0.44 mg/m<sup>3</sup>). The latter were much more similar to the estimated outside background levels (0.13-0.3 mg/m<sup>3</sup>) determined for samples taken on the roof of the DOL motor pool. There also appear to be differences in the estimated particle size distributions. The MMAD of the raw, diluted exhaust ranged from 0.2 to 0.5  $\mu$ m, while the particle size distribution measured at DOL, DISCOM, and Fourth Engineering Bn motorpools during the 1986 sampling trip (see next section) were found to be bimodal, with a small particle mode at 0.4-0.9  $\mu$ m, and a large particle mode at 3-4  $\mu$ m. Although the latter mode could represent additional sources of particles to the workplace atmosphere, coagulation or agglomeration of the diesel exhaust particles contributes to such larger particle modes (33).

The organic components of the workplace atmosphere also were found to differ from those of diesel engine exhaust and also the ambient outside background. Figure 9 compares the major chromatographable particulate organics in the 4/68th Armored Division motor pool air and in ambient outside air. These can be compared with M-60 tank exhaust in Figure 5. Quantitative data for the major particulate organics are listed in Tables 4, 5, and 8. The diesel engine exhaust is an obvious major contributor to the particulate organics in the workplace atmosphere, but there also are major quantitative differences in the distributions or relative ratios of components. The most obvious difference is that the distribution in the diesel engine exhaust peaked at C<sub>10</sub> or C<sub>20</sub>, while in the motor pool garages, the peak was at C<sub>20</sub> to C<sub>23</sub>. This slightly higher distribution for the workplace atmosphere may indicate additional sources. However, it also could be an artifact of the longer sampling time required for the collection of the workplace air samples, which would cause more sublimation of semivolatile organic compounds. The concentrations of the organics calculated as both particulate and air concentrations are higher in the exhaust than in the TSP, except for the particulate concentrations in the Armored motor pool sample 25-A-1. In general, the particulate organics concentrations were up to 20-fold greater in the exhaust than in the workplace air, but the differences do not appear as great for the higher molecular weight (and less prone to sublimation) organics, including the BaP and 1-NP (Tables 6 and 9). This observation again suggests that some of the quantitative differences could be a sampling artifact. The major organic compounds in the workplace atmosphere were more concentrated than those in the ambient outside air by factors of ca. 2 to 100, indicating the accumulation of organic matter in the former. For these two types of samples, the sampling volumes were similar, and differences in composition are more confidently interpreted.

Figure 8 and Table 7 compare the corresponding data for the vapor phase organic compounds. The contributions of the diesel engine exhaust to the workplace atmosphere are evident in the higher molecular weight range (> ca. C<sub>11</sub>) of the workplace air. However, the workplace air contained a more complex and more concentrated (relative to the other constituents) mixture of components below ca. C<sub>11</sub>. The diesel engine exhaust contained organics levels up to 100-times higher than for the

Table 8. Comparison of Major Particulate Phase Organic Compounds  
in the Motor Pool Workplace Atmosphere and Ambient Outside Background  
in September, 1984

Compound	Concentration, $\mu\text{g/g TSP}$					
	4/68th Armored		Engineering		Background	
	Mtr. Pool		Mtr. Pool		(DIO Roof)	
	26-A-1	25-A-1	24-E-1	25-E-3	26-D-1	25-D-1
C <sub>19</sub>	47	4,000	52	60	30	17
C <sub>20</sub>	75	4,800	72	100	41	23
C <sub>21</sub>	230	4,200	140	130	60	26
C <sub>22</sub>	380	3,100	210	160	48	20
C <sub>23</sub>	370	2,100	220	180	54	17
C <sub>24</sub>	190	1,200	150	150	37	11
C <sub>25</sub>	160	920	130	140	42	-
C <sub>26</sub>	78	420	50	63	20	-
C <sub>27</sub>	40	310	35	-	33	-
C <sub>28</sub>	50	270	30	-	22	-
C <sub>29</sub>	110	260	38	54	63	5
C <sub>30</sub>	86	-	24	-	30	-
C <sub>31</sub>	110	-	26	-	59	-

Compound	Concentration, $\text{ng/m}^3$					
	4/68th Armored		Engineering		Background	
	Mtr. Pool		Mtr. Pool		(DIO Roof)	
	26-A-1	25-A-1	24-E-1	25-E-3	26-D-1	25-D-1
C <sub>19</sub>	10	160	23	14	3.7	4.6
C <sub>20</sub>	17	180	31	23	5.2	6.1
C <sub>21</sub>	51	170	61	30	7.5	7.0
C <sub>22</sub>	85	120	91	36	6.0	5.3
C <sub>23</sub>	82	82	94	43	6.8	4.6
C <sub>24</sub>	42	47	65	36	4.6	3.0
C <sub>25</sub>	36	37	56	31	5.2	-
C <sub>26</sub>	17	17	22	15	2.5	-
C <sub>27</sub>	10	12	15	-	4.2	-
C <sub>28</sub>	12	11	13	-	2.8	-
C <sub>29</sub>	24	10	16	13	7.9	1.4
C <sub>30</sub>	19	-	10	-	3.8	-
C <sub>31</sub>	24	-	11	-	7.4	-

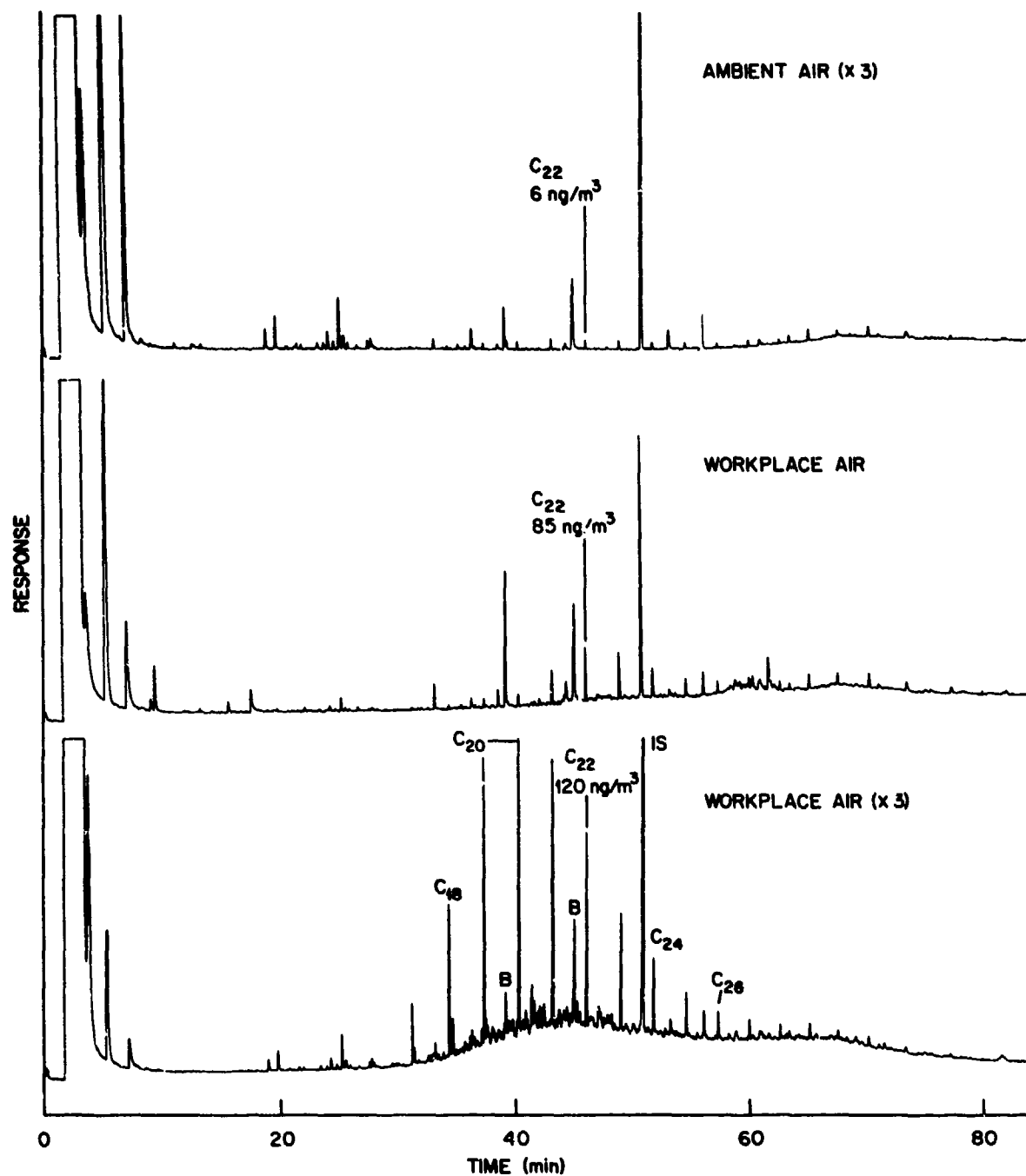


Figure 9. Comparison of the Major Chromatographable Organic Particulate Phase Compounds in Ambient Air and the Workplace Atmosphere at the 4/68th Armored Brigade Motor Pool (For GC conditions, see Figure 5)

Table 9. Comparison of Benzo(a)pyrene and 1-Nitropyrene Determinations in Workplace and Ambient Outside Air with Literature Data for Rural and Urban Ambient Air

Filter Sample	Description	Benzo(a)pyrene		1-Nitropyrene	
		µg/g TSP	ng/m <sup>3</sup>	µg/g TSP	ng/m <sup>3</sup>
26HV Area D-1	DIO Roof (Bkgd)	2.4	0.30	< 0.4	< 0.05
26HV Area A-1	4/68th Ar. Mtr. Pl.	16	3.5	4.5	1.0
----- Literature -----					
Ref. 34	30 Rural Samples	-	0.6 ± 0.2	-	0.009 ± 0.005
Ref. 35	Rural Samples	-	0.11 to 3.6	-	< 0.001 to 0.04
Ref. 18	Urban Area	6.3 to 11	-	0.2 to 0.6	0.02 to 0.03
Ref. 24	Industrial Area	-	-	0.22	0.02
-	Urban Areas	-	0.1 to 3.5	-	-

workplace air, and particularly for the aromatic compounds and the less volatile of the vapor phase compounds. The latter would be less sensitive to differences in the sampling conditions, and they suggest additional sources such as fuel vapors. We have identified these compounds in the vapors of diesel fuel (7). Benzene, a toxic aromatic compound, was found at concentrations of 91 and 220  $\mu\text{g}/\text{m}^3$  in the engine exhaust, versus 1.4 to 5.5  $\mu\text{g}/\text{m}^3$  in the workplace and 0.9  $\mu\text{g}/\text{m}^3$  in the outside air.

The main conclusions of this portion of the study are that the particulate and vapor phase organics in the motor pool workplace atmosphere are considerably more concentrated than in the ambient outside air, and that diesel engine exhaust is a major contributor to the former. The composition of engine exhaust, and hence its toxicology and that of the workplace atmosphere may be affected by engine lubricants and fuel as well as the engine condition, speed and load. Additional sources and chemical transformations of the organics also are possible contributors to the chemistry of the workplace air.

## DETAILED ORGANIC CHEMICAL CHARACTERIZATION OF THE MOTOR POOL WORKPLACE ATMOSPHERE

A second sampling trip to Fort Carson, CO was carried out in September and October of 1986 to collect samples for a more detailed analysis of the workplace atmospheres in three motor pool garages: DISCOM, DOL, and the Fourth Engineering Bn. Both time resolved (TR) and time averaged (TA) samples were collected at multiple locations in these facilities to allow an assessment of the temporal and spatial variability of the workplace atmospheric composition. In the same time frame, the U.S. Army Environmental Hygiene Agency (AEHA, Aberdeen Proving Ground, MD) conducted sampling and on-site measurements for contaminants recommended by the Occupational Safety and Health Administration (OSHA) and the American Conference of Governmental Industrial Hygienists (ACGIH). The detailed results of the ORNL study are contained in the Appendix. The AEHA results were reported separately (36). The gross physical characteristics, organic chemical composition, and the variability of the concentrations of these parameters in the workplace atmosphere are needed to define the composition and limits of exposure of the personnel and to serve as an input to the design of exposure conditions for animal toxicology experiments.

### Gross Physical Characterization

A detailed listing of the gross physical characteristics of TSP concentrations and particle size distributions plus the total  $C_1$ - $C_8$  hydrocarbons analyses is included in Appendix Table A-2. Except for one source sample (painting,  $21 \mu\text{g}/\text{m}^3$ ), all the TSP measurements were  $<550 \mu\text{g}/\text{m}^3$ , and most were  $<300 \mu\text{g}/\text{m}^3$ . DISCOM had the highest TSP levels during this study; the TA samples ranged from 155 to  $385 \mu\text{g}/\text{m}^3$  and the TR samples varied from 109 to  $370 \mu\text{g}/\text{m}^3$ . The contribution of work activities is evident from the much lower values of 16 to  $70 \mu\text{g}/\text{m}^3$  found in overnight sample collections. The TSP in an ambient outside air sample collected at DOL during a daytime workshift was  $48 \mu\text{g}/\text{m}^3$ . The ca. hourly TR samples tended to be highest during the early morning hours when vehicles were being moved into the garages and their engines were being warmed up. In general, vehicle exhaust collection devices were not used in the garage, and the main ventilation was by opening the motor pool garage doors.

The TSP at DOL was lower than at DISCOM, and slightly above that at the Fourth Engineering Bn. At DOL, the TSP in TA samples ranged from 21 to  $148 \mu\text{g}/\text{m}^3$  during workhours, and 15-34  $\mu\text{g}/\text{m}^3$  overnight. At the Fourth Engineers, the TSP was very low on the first day of sampling, September 30 (TR was 25-67  $\mu\text{g}/\text{m}^3$  and TA was 12-36  $\mu\text{g}/\text{m}^3$ ). This undoubtedly was a result of no vehicles being run in the garage on that day. The TR TSP concentrations decreased serially during the day (the TSP in the TR samples was 67 [0859-1005 hrs], 61 [1009-1109 hrs], 61 [1110-1217 hrs], 37 [1219-1319 hrs], and 25  $\mu\text{g}/\text{m}^3$  [1323-1536 hrs]). The air sampling

rate was too low to have significantly removed particulate matter from the atmosphere. The decay in TSP probably reflects building ventilation and the lack of running vehicles that day. The much higher TSP (TR was 97-546  $\mu\text{g}/\text{m}^3$  and TA was 155-220  $\mu\text{g}/\text{m}^3$ ) on the second day of sampling reflects normal operating activity in the garage.

The time weighted average (TWA) calculated for two sets of TR samples collected during the same time interval as were the TA samples tended to be slightly higher, but not unreasonably more, than the TA results. The TWA calculated for the TR TSP at the DISCOM middle sampling location on September 24 was 274  $\mu\text{g}/\text{m}^3$ , while the TA sample was 197  $\mu\text{g}/\text{m}^3$ . Similarly, for the Fourth Engineering north wheel bay, the TWA of the TR samples collected in the north corner was 46  $\mu\text{g}/\text{m}^3$  versus the TA samples of 36 (east corner) and 18 (west corner)  $\mu\text{g}/\text{m}^3$ . The differences probably reflect the localized nature of the major emission sources (vehicle exhaust plumes) and the difficulties in collecting exactly identical samples.

The particle size distributions of the samples were found to be bimodal, and no significant differences were detected among the three motor pools sampled (Appendix Table A-4). The small particle mode was 0.4-0.5  $\mu\text{m}$  MMAD, and the large particle mode was 3-4  $\mu\text{m}$  MMAD. The small particle mode is very similar to the MMAD of raw diesel engine exhaust (see previous section), indicating that the latter is a major source of particulates. The large mode probably represents coagulation or agglomeration of the raw engine exhaust (33) as well as other source contributions.

Total gas phase  $\text{C}_1$ - $\text{C}_8$  hydrocarbons were determined by gas-solid chromatography of gas bulb samples returned to the laboratory. The results were very narrowly spread over 4.5 to 6.6 ppm (vol/vol) (Appendix Table A-2), and were not particularly elevated over the 2.3 ppm measured in an ORNL laboratory air sample. There was no apparent correlation of the total gas phase hydrocarbons with the TSP. This finding may be a result of the different diffusion rates and resulting dispersion of gases versus particles.

#### Detailed Organic Chemical Characterization of the Workplace Atmosphere at DISCOM

The particle phase filters and vapor phase solid sorbent traps were subjected to the same analytical procedures as were used for the first set of samples, except that a greater number of PAH dermal tumorigens was measured by the GC-MS. Nitro-substituted PAH also were measured; however, the agreement between the measured value and the certified value for 1-NPy in NBS SRM 1650 Diesel Exhaust Particulates (Appendix Table A-2) was poor, and those data are not considered valid. A detailed characterization of the particulate phase organic compounds present in the DISCOM workplace atmosphere at the middle sampling location on September 24 (sample DIS-24-TA-3) is presented by the GC-MS total ion current chromatogram shown at the bottom of Figure 10, and in the inventory Table . The data in the table include those for the TA



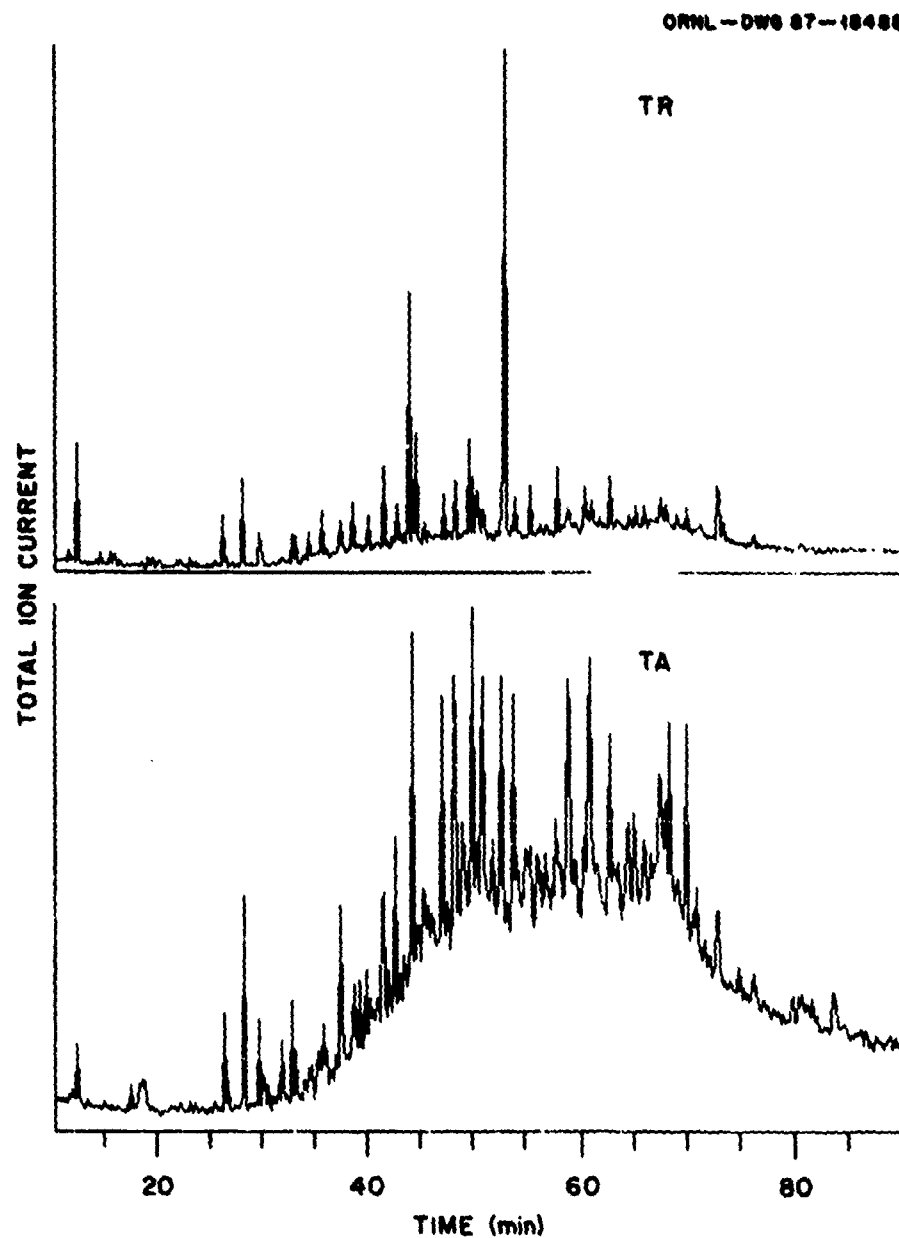


Figure 10. Comparison of the GC-MS Total Ion Current Chromatograms of the Major Particulate Phase Organic Compounds in Time Resolved and Time Averaged Samples of the Workplace Atmosphere at DISCOM (See Table 10 for compound identification and quantification) (For GC conditions, see Figure 5, except He instead of H<sub>2</sub> carrier gas)

sample DIS-24-TA-3 (0855-1559 hrs) and the TWAs calculated for the TR samples DIS-24-TR-1 through -TR-5 (0854-1611 hrs). The workplace atmosphere was found to be a very complex mixture of both aliphatic and aromatic compounds. The n-alkanes were the most concentrated species. They ranged from  $C_{12}$  to at least  $C_{33}$ , and were found at concentrations up to 190  $\mu\text{g/g}$  of TSP (corresponding to a concentration of 37  $\text{ng/m}^3$  in the workplace air) in the TA sample. Pristane and phytane also were identified. These two distinctive branched alkanes also were among the alkanes identified in the diesel engine exhaust (see last section) and in the diesel fuel (7). Of greater toxicological importance is the finding of relatively high concentrations of PAH. Quantitative measurements of several 4- to 6-ring PAH dermal tumorigens are included in Table 9. The concentrations of many of these PAH were as high as those of the n-alkanes. BaP was 65  $\mu\text{g/g}$  (13  $\text{ng/m}^3$ ), and benzo[ghi]perylene was 160  $\mu\text{g/g}$  (32  $\text{ng/m}^3$ ) in the TA sample. Most of the other PAH measured were at least as concentrated as BaP. The relatively high concentrations of these PAH allowed them to be detected readily in the qualitative GC-MS of the crude filter extracts; their chromatographic peaks in Figure 10 are identified by retention time and listed in Table 10. This situation is considerably different from that of the ambient outdoor air sample, in which the PAH were ca. 10-fold lower in concentration than the alkanes. As will be described in the following subsection, these relatively high levels of PAH were not found at the two other motor pool garages.

A curious observation was that the concentrations of the smaller ( $< \text{ca. } C_{23}$ ) alkanes in the TR particulate samples were higher than those in the corresponding TA particulate sample for DISCOM on September 24, 1986. The alkanes are more prominent versus the P-d in the TR sample shown at the top of Figure 10 (DIS-24-TR-5) than in the TA sample at the bottom of the Figure. The quantitative data (Table 10) bear this out. The data show that below  $C_{24}$ , the TWA of the TR samples is higher, but for larger (less volatile) alkanes and PAH, the differences are minimal. This suggests that some preferential loss of the lower alkanes occurred during the longer TA sampling. The PAH are more polarizable than the nonpolar alkanes, and their losses by sublimation from the filter media may be less than those for alkanes with similar boiling points and vapor pressures in their pure solid state (not sorbed on particulates), i.e., the PAH may be sorbed more strongly to the particulates than are the alkanes. We have observed this preferential sorption of aromatics versus aliphatics with coal combustion stack ash (37). To our knowledge, this is the first report of a comparison of the results of organic analyses of short- and long-term air sampling in this type of workplace atmosphere. It illustrates the problems associated with particulate organics sampling by filtration, and the potential bias in data based upon long-term sampling periods. In some cases, however, such long sampling times are required to provide sufficient sample for analysis.

Table 10. Inventory of Particulate Organic Compounds Identified in the Workplace Atmosphere in DISCOM in September 24, 1988

Retention Time, min. <sup>a</sup>	m/z <sup>b</sup>	Identification <sup>c</sup>	Concentration <sup>d</sup>			
			IA		TWA of TR	
			µg/s	ng/m <sup>3</sup>	µg/s	ng/m <sup>3</sup>
12.2	57	n-Dodecane	-	-	-	-
26.3	149	Diethylphthalate	-	-	-	-
26.7	57	n-Hexadecane	3.8	0.8	17	5
28.3	99	Tributylphosphate	-	-	-	-
29.9	71	n-Heptadecane	25	4.9	62	16
30.1	71	Pristane	-	-	19	4.7
32.0	178	Phenanthrene	-	-	-	-
33.0	57	n-Octadecane	14	2.8	57	14
33.3	57	Phytane	24	4.7	58	15
35.5	180	C <sub>2</sub> -Acenaphthene	-	-	-	-
36.0	71	n-Nonadecane	29	5.7	140	34
37.6	149	Dibutylphthalate	-	-	-	-
38.8	57	n-Eicosane	51	10	150	38
39.0	194	C <sub>2</sub> -Fluorene	-	-	-	-
39.3	198	C <sub>5</sub> -Naphthalene	-	-	-	-
40.0	202	Fluoranthene	-	-	-	-
40.6	202	Acphenanthrylene	-	-	-	-
41.4	202	Pyrene	-	-	-	-
41.6	71	n-Heneicosane	150	30	291	77
42.0	206	C <sub>2</sub> -Phenanthrene	-	-	-	-
44.4	71	n-Docosane	190	37	300	77
47.1	71	n-Tricosane	130	26	190	50
48.3	149	Dibutylbenzylphthalate	-	-	-	-
49.0	226	Benzo(ghi)fluoranthene	-	-	-	-
49.9	71	n-Tetracosane	120	23	110	28
50.1	234	C <sub>4</sub> -Phenanthrene	-	-	-	-
50.7	228	Benzo(a)anthracene	88	13	59	16
-	228	Chrysene <sup>e</sup>	100	20	107	28
50.8	240	C <sub>1</sub> -Benzo(ghi)fluoranthene	-	-	-	-
51.8	230	C <sub>2</sub> -Pyrene	-	-	-	-
52.6	57	n-Pentacosane	84	17	70	19
52.9	191	2,2'-Methylenebis(4-ethyl, 6-t-butylphenol) <sup>f</sup>	-	-	-	-
53.6	149	Octylphthalate	-	-	-	-
54.1	242	C <sub>1</sub> -Chrysene	-	-	-	-
54.7	240	Cyclopentachrysene	-	-	-	-
55.2	57	n-Hexacosane	88	17	52	14
57.8	71	n-Heptacosane	82	12	61	17
58.6	149	Phthalate	-	-	-	-
58.8	252	Benzo(b/j)fluoranthenes	140	27	73	17
-	252	Benzo(k)fluoranthene <sup>g</sup>	28	6	18	4
59.4	71	n-Octacosane	42	8.3	29	7.7
59.6	252	Benzo(a)fluoranthene	24	5	25	6
60.6	252	Benzo(e)pyrene	48	9	57	14
60.9	252	Benzo(a)pyrene	65	13	83	20
61.5	252	Perylene	-	-	-	-

<sup>a</sup>Figure 10.

<sup>b</sup>Base ion or apparent molecular ion.

<sup>c</sup>GC-MS of DIS-24-TA-3.

<sup>d</sup>Concentration in DIS-24-TA-3 (0855-1559 hrs) and TWA of DIS-24-TR-1 through -TR-5 (0854-1811 hrs) except for PAH (-TR-2 missing).

<sup>e</sup>Identified in separate GC-MS analysis specific for PAH.

<sup>f</sup>Tentative identification from spectral matching.

Table 10. Inventory of Particulate Organic Compounds Identified  
in the Workplace Atmosphere in DISCOM in September 24, 1986  
(Cont'd)

Retention Time, min. <sup>a</sup>	m/z <sup>b</sup>	Identification <sup>c</sup>	Concentration <sup>d</sup>			
			TA		TWA of TR	
			µg/g	ng/m <sup>3</sup>	µg/g	ng/m <sup>3</sup>
62.8	57	n-Nonacosane	99	20	75	21
63.5	266	C <sub>1</sub> -Benzopyrene	-	-	-	-
64.2	254	C <sub>2</sub> -Benzo(ghi)fluoranthene	-	-	-	-
64.4	264	Alkyl-PAH	-	-	-	-
65.1	57	n-Triacontane	50	10	33	10
65.8	191	Heterocyclic	-	-	-	-
67.4	57	n-Henotriacontane	130	25	84	23
-	276	Dibenz(a,j)anthracene <sup>e</sup>	16	3	11	3
67.8	276	Indeno(123-cd)pyrene	70	14	140	34
68.3	276	Dibenz(a,c/a,h)anthracenes	5	1	10	2
68.7	278	PAH	-	-	-	-
69.2	57	n-Dotriacontane	47	9.2	34	9.0
69.8	276	Benzo(ghi)perylene	160	32	120	26
70.8	276	Anthanthrene (?)	-	-	-	-
72.8	-	n-Tritriacontane	44	8.6	35	9.1
74.7	268	Alkyl-PAH	-	-	-	-

The vapor phase organic compounds collected at the DISCOM mezzanine on September 24, 1986 (DIS-24-TA-2) are qualitatively compared with those from the ambient outside background in Figure 11. The compounds are identified in Table 11. As observed previously (Figure 8) for the diesel engine exhaust and other motor pool workplace atmosphere samples collected in 1984, the major constituents were n-alkanes from C<sub>7</sub> through C<sub>16</sub>, benzene, and a series of alkyl benzenes extending through C<sub>4</sub>-substitution. Naphthalene also was detected. The workplace air sample was more enriched in these constituents than was the outside air sample. The TWA air concentrations of several vapor phase organic compounds calculated from TR samples collected September 23 and 24 at the DISCOM middle location are listed in Table 12. The thermal-desorption GC analytical methodology for the combination traps was very similar to that used for the Tenax traps from the first Fort Carson trip, except that a Tekmar thermal-desorption unit was employed, and the capillary column had a DB-5 bonded phase. The range of compounds desorbed with this equipment was limited to the xylenes, while higher-boiling constituents were desorbed in the earlier analysis. Benzene was found at 5.5 to 6.0 µg/m<sup>3</sup>, and even higher concentrations of toluene (36 and 49 µg/m<sup>3</sup>) and other aromatics were measured. These concentrations are somewhat higher than those determined previously for two other motor pool garages at Fort Carson (Table 7), indicating the greater contamination of this workplace atmosphere at the time of sampling.

The degree of variability in the concentrations of the constituents comprising the workplace atmosphere must be determined to define the limits of potential workplace exposure. The spatial and temporal variability were evaluated in this study.

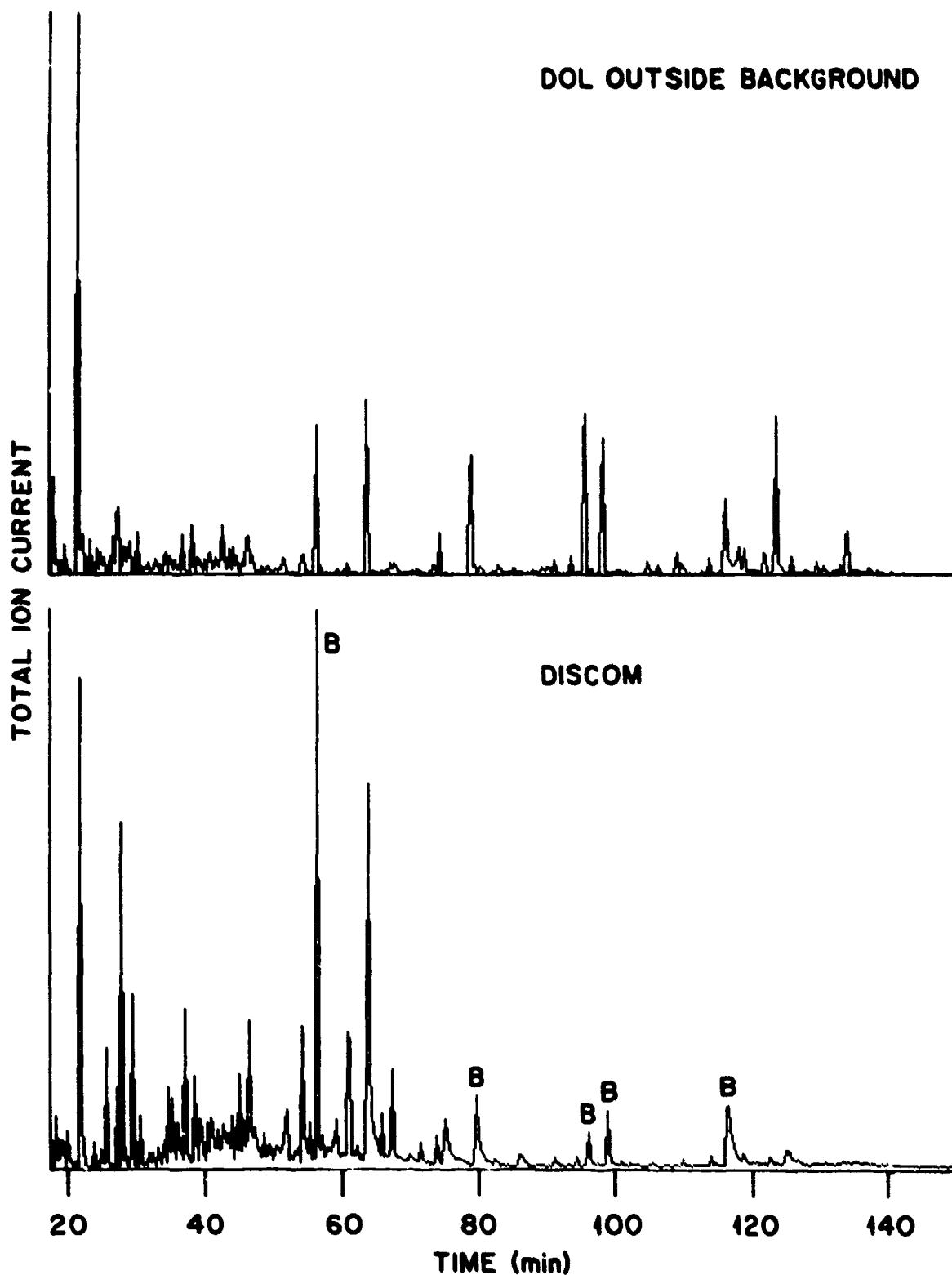


Figure 11. Comparison of the GC-MS Total Ion Current Chromatograms of the Major Vapor Phase Organic Compounds in Outside Ambient Air (4.6 L) and the Workplace Atmosphere at DISCOM (4.6 L) (See Table 11 for compound identification. B indicates compound found in blank sample. GC conditions: 30 m x 0.25 mm ID fused silica with 0.25  $\mu$ m DB-5 bonded phase, temperature programmed from 25°C [20 min isothermal hold] to 250°C at 2°/min.)

Table 11. Qualitative Inventory of Vapor Phase Organic Compounds  
Identified in the Workplace Atmosphere at DISCOM on September 24, 1987

Retention Time, min. <sup>a</sup>	Identification <sup>b</sup>	Retention Time, min.	Identification
16.8	n-Pentane	43.0	C <sub>4</sub> -Benzene
17.4	n-Hexane	43.5	Alkane
18.3	Benzene	44.0	C <sub>4</sub> -Benzene
19.3	n-Heptane	44.8	C <sub>4</sub> -Benzene
19.8	C <sub>7</sub> -Olefin	45.7	C <sub>11</sub> -Olefin
21.7	Toluene	46.0	C <sub>4</sub> -Benzene
22.2	C <sub>8</sub> -Olefin	46.4	n-Undecane
23.7	n-Octane	46.9	C <sub>4</sub> -Benzene
27.2	Ethyl Benzene	47.2	C <sub>4</sub> -Benzene
27.7	m- and/or p-Xylene	48.3	C <sub>11</sub> -Olefin
28.3	Alkane	51.4	Alkane
29.3	o-Xylene	51.6	Naphthalene
30.4	n-Nonane	54.2	n-Dodecane
31.7	C <sub>3</sub> -Benzene	54.4	Alkane
32.8	C <sub>8</sub> -Olefin	55.1	Alkane
33.0	Alkane	58.5	Alkane
34.0	C <sub>3</sub> -Benzene	58.9	Alkane
34.7	C <sub>3</sub> -Benzene	59.1	Alkane
35.2	C <sub>3</sub> -Benzene	60.8	n-Tridecane
35.4	Alkane	62.0	Alkane
36.0	C <sub>3</sub> -Benzene	64.9	Alkane
37.1	C <sub>3</sub> -Benzene	65.8	Alkane
38.3	n-Decane	67.2	n-Tetradecane
39.3	C <sub>3</sub> -Benzene	71.3	Alkane
40.1	Alkane	73.7	Alkane (n-C <sub>15</sub> ?)
40.8	Alkane	79.6	n-Hexadecane
40.9	Alkane		
41.9	C <sub>4</sub> -Benzene		
42.5	C <sub>4</sub> -Benzene		

<sup>a</sup>See Figure 11.

<sup>b</sup>In sample DIS-24-TA-2.

Table 12. Time Weighted Averages of Vapor Phase Organic Compounds  
in Time Resolved Samples Collected in the Workplace Atmosphere  
at DISCOM on September 23 and 24, 1986

Compound	Concentration, $\mu\text{g}/\text{m}^3$	
	AM, 9/23/86 <sup>a</sup>	PM, 9/24/87 <sup>b</sup>
Hexane	13	13
Benzene	5.5	6.0
Heptane	11	9.9
Toluene	49	36
Octane	6.9	4.1
Ethyl Benzene	19	9.3
m/p-Xylenes	220	71

<sup>a</sup>0907-1242 hrs calculated from DIS-23-TR-1 through -TR-3.

<sup>b</sup>1120-1611 hrs calculated from DIS-24-TR-3 through -TR-5.

### Spatial Variation in Composition

Spatial variability in the composition of the workplace atmosphere was investigated by collecting and analyzing air samples at different motor pool facilities (ie, DISCOM, DOL, and Fourth Engineering Bn) and also at different locations within a single facility during the same time period. As graphically illustrated by the gas chromatograms of the major chromatographable particulate phase organics (Figure 12) from the three motor pools sampled during the 1986 trip, the distributions of organic compounds within the particulate were quantitatively very different. The samples from the three facilities all shared many of the same constituents, but the concentrations were different. In addition, the distribution and intensity of the unresolved baseline rise exhibited by the chromatogram was quite different for the three facilities. At the time these samples were collected, the highest concentrations and complexity were observed at DISCOM, followed by DOL, and the Fourth Engineering Bn motor pools. Quantitative differences among the samples from the three facilities are shown by the data for indicators of atmospheric contamination listed in Table 13. The indicators are representative of the full body of characterization contained in the Appendix Tables A-2 through A-21 and they include TSP, benzene (vapor phase constituent), n-tetracosane (a major particulate phase constituent which is not affected by long sampling periods), and BaP (a tumorigenic particulate phase constituent). Included in the tabulation are data for the ambient outside air (the background) and diesel engine exhaust from an M-60 tank (a major workplace atmospheric contamination source). Except for the air concentrations of TSP and BaP at the Fourth Engineering Bn on September 30, the samples collected in the motor pool garages were much more contaminated than the outside background. They also were much less concentrated than in diesel engine exhaust. Two main differences among the facilities were that the air concentrations of these indicators were different by factors ranging from ca. 4 to 50, and the concentrations of the components in the TSP also varied over an order of magnitude, i.e., both the air concentrations of the contaminants and the composition of the particles were different at each of the three facilities. The relatively high concentrations of BaP at DISCOM could reflect elevated diesel engine emissions, but the n-tetracosane concentration appears lower than would be expected from a major engine exhaust contribution. An important conclusion is that diesel engine exhaust is not a suitable surrogate for defining the potential hazards of exposure to workplace atmospheres. Contributions from other emission sources and from transformations of emitted compounds may be important.

Differences in organic compound distribution among suspended and settled particles, diesel engine exhaust particulates, and outside ambient air particulates are compared in more detail in Table 14. The data show that the diesel engine exhaust particles from an M-60 tank were different from the DISCOM TSP in that the former had much higher concentrations and a different distribution of n-alkanes, but a lower concentration of BaP. Both were quite different from the outside ambient air. The suspended and settled particles from DISCOM are an

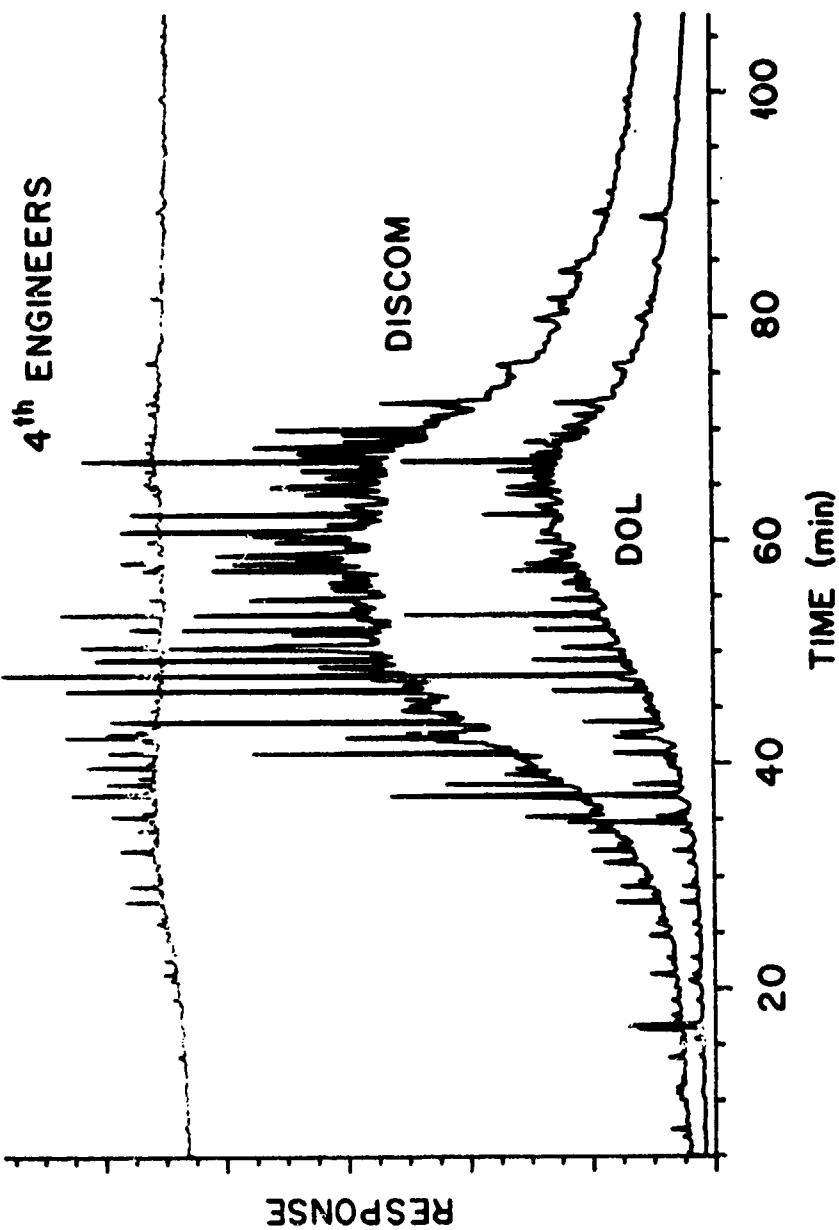


Figure 12. Comparison of the Chromatographable Major Organic Particulate Phase Organics from the Workplace Atmospheres at the Fourth Engineering Bn, DISCOM, and DOL Motor Pools (For GC conditions, see Figure 5)



Table 13. Comparison of Contamination Indicators for Three Motor Pool Workplace Atmospheres, Outside Ambient Air, and Diesel Engine Exhaust

Location	Indicator Concentration <sup>a</sup>					
	TSP, <sub>3</sub> μg/m <sup>3</sup>	Benzene, μg/m <sup>3</sup>	n-Tetracosane		BaP	
			ng/m <sup>3</sup>	μg/g	ng/m <sup>3</sup>	μg/g
DISCOM <sup>b</sup>	270	5.5 <sup>c</sup>	28	110	20 <sup>d</sup>	83 <sup>d</sup>
DOL <sup>e</sup>	110	NA	7.4	67	3.2	29
4th Engineers <sup>f</sup>	46	NA	12	230	0.4	7.1
Outside Background <sup>g</sup>	48	NA	3.4	71	0.4	8.0
Diesel Engine Exhaust <sup>h</sup>	2,800	220	4,200	1,500	48	17

<sup>a</sup>NA = not analyzed

<sup>b</sup>TWA of DIS-24-TR-1 through -TR-5 (0584-1611), except as noted.

<sup>c</sup>TWA of DIS-24-TR-3 through -TR-5 (1120-1611).

<sup>d</sup>Same as B, except -TR-2 was missing.

<sup>e</sup>DOL-25-TA-3 (0653-1531).

<sup>f</sup>TWA of ENG-30-TR-1 through -TR-5 (0859-1536).

<sup>g</sup>DOL-Outside Background, 9/25/86.

<sup>h</sup>M-60 tank, 25-A-1.

interesting comparison because the latter could represent a long-term integrated and aged sample of the larger, settleable particles from the former. The TWA of TSP samples was calculated from the data for two TA samples collected on the mezzanine at DISCOM where the settled dust sample was taken. The results for the n-alkanes are remarkably similar, but the PAH concentrations in the TSP are much higher than those in the settled dust. This observation suggests that the PAH in the TSP are associated to a greater extent with the very fine, sub-μm particles which do not settle out and which are much more readily transported in the atmosphere. It also could represent a settled particulate contribution from infiltrating outside air. These results show that both diesel engine exhaust particulates and the settled dust would not be a suitable surrogate for the workplace atmosphere particulates in toxicity studies.

Variation of the workplace atmospheric composition within a single facility was evaluated by collecting samples simultaneously at different locations within the DISCOM and also the Fourth Engineering Bn motorpools. Table 15 presents the analytical data for the contamination indicator concentrations at the DISCOM mezzanine, middle, and west sampling locations, and for two corners of the west track bay and the north wheel bay of the Fourth Engineering Bn motor pool. The variability among these parameters for different locations within the same facility was less than a factor of 10, and was not as great as for the facility-to-facility differences. However, some other constituents (e.g., n-docosane, see Appendix) were observed to vary over an order of magnitude.

Table 14. Comparison of the Organic Compound Composition of Settled and Suspended Particulates, Diesel Engine Exhaust, and Outside Ambient

Compound	Concentration <sup>a</sup> in Particles, $\mu\text{g/g}$			
	Settled Particles <sup>b</sup>	Suspended Particles <sup>c</sup>	M-60 Exhaust <sup>d</sup>	Outside Air <sup>e</sup>
n-Tetracosane	38	39	1,500	71
n-Pentacosane	15	36	1,000	55
n-Hexacosane	19	22	350	21
n-Heptacosane	19	20	150	29
n-Octacosane	11	11	< 100	P
n-Nonacosane	21	25	< 100	43
n-Triacontene	19	15	< 100	31
Benz(a)anthracene	0.5	110	NA	4.9
Chrysene	2.1	150	NA	1.2
Benzo(e)pyrene	1.2	65	NA	9.4
Benzo(a)pyrene	0.7	130	17	8.0

<sup>a</sup>NA = not analyzed.

<sup>b</sup>DISCOM dust sample collected from the mezzanine.

<sup>c</sup>TWA of DIS-24-TA-1 and -TA-2.

<sup>d</sup>M-60 tank exhaust sample 25-A-1.

<sup>e</sup>Outside ambient air sample DOL-Outside Background.

Table 15. Spatial Variation of Workplace Atmospheric Contamination Indicators for DISCOM and Fourth Engineers Bn Motor Pools

Location	Time	Indicator Concentration <sup>a</sup>		
		TSP, μg/m <sup>3</sup>	n-C <sub>23</sub> , ng/m <sup>3</sup>	BaP, ng/m <sup>3</sup>
DISCOM:				
Mezzanine	0843-1257	250	50	41
	1301-1541	250	22	18
Middle	0855-1559	200	23	13
West	0900-1621	290	24	7.9
ENG:				
Wst Trk (SW)	0914-1435	15	4.2	0.2
Wst Trk (NE)	0919-1452	12	5.7	0.2
Nth Whl (W)	0853-1524	18	8.1	0.3
Nth Whl (E)	0845-1509	36	NA	NA

<sup>a</sup>NA = not analyzed

### Temporal Variation in Composition

The composition of the workplace atmosphere is not expected to be static, but rather to change with time as contaminant sources initiate and cease their emissions, as the emissions are dispersed in the facility, and as they are removed by the facility ventilation. Opening and closing of garage doors was observed during the sampling trips to have a major influence upon dilution and removal of exhaust fumes. The temporal variation in the composition of the workplace atmospheric contamination was tracked by collecting ca hourly sequential TR samples at single locations within the DISCOM and Fourth Engineers motor pools. The samples collected at a single location were found to be much more uniform than those from different motor pools, as would be expected from the greater uniformities in the ventilation and the nature and load of the work activities. These similarities are evident in the gas chromatograms (Figure 13) of the major chromatographable particulate organic compounds from three filter samples collected on September 24, 1986, at the middle sampling location of DISCOM. These chromatograms show a much greater consistency in composition than those of samples from different facilities, illustrated in Figure 12. The quantitative measurements of indicator compounds listed in Table 16 for two motor pools show peaks in the contaminant concentrations in the mid- or early morning, and shortly after noon. These peaks may result from the personnel bringing vehicles into the motor pools and the warming up of engines before repairs or tuning. The noon dip in concentrations is undoubtedly from the decrease in activity during the lunch break. The overall variation in concentrations was ca. 2 to 7-fold for the TSP and the major organic compound, and 2 to 15-fold for the BaP, especially where it was a trace level ( $<1 \text{ ng/m}^3$ ) constituent. The concentration changes for benzene over a shorter range of time were ca. 3-fold. As would be expected from the cessation of work activities at the end of the day, the contamination levels during the overnight period dropped 3 to 9-fold for TSP and n-tetradocosane, and ca. 30-fold for BaP. The lesser drop in the former probably reflects the contribution of infiltrating outside air particulates.

The day-to-day variations in the workplace atmosphere composition over longer (ca 3 to 8 hr) integrated intervals at specific locations is addressed by the indicator data in Table 17. The magnitude of the day-to-day variability was found to be very similar to that for the hourly variability, viz., ca. 3-fold for major constituents and up to 10-fold for trace-level constituents such as BaP. Inclusion of overnight samples in the comparison extends the variation to a factor of 10 and greater.

### Comparison with AEHA Results

The results for the AHEA measurements of dust (TSP), NO, NO<sub>2</sub>, SO<sub>2</sub>, three nitrosamines (N-nitrosodimethylamine, N-nitrosodiethylamine, and N-nitroso-n-propylamine), and CO were reported separately (36). In

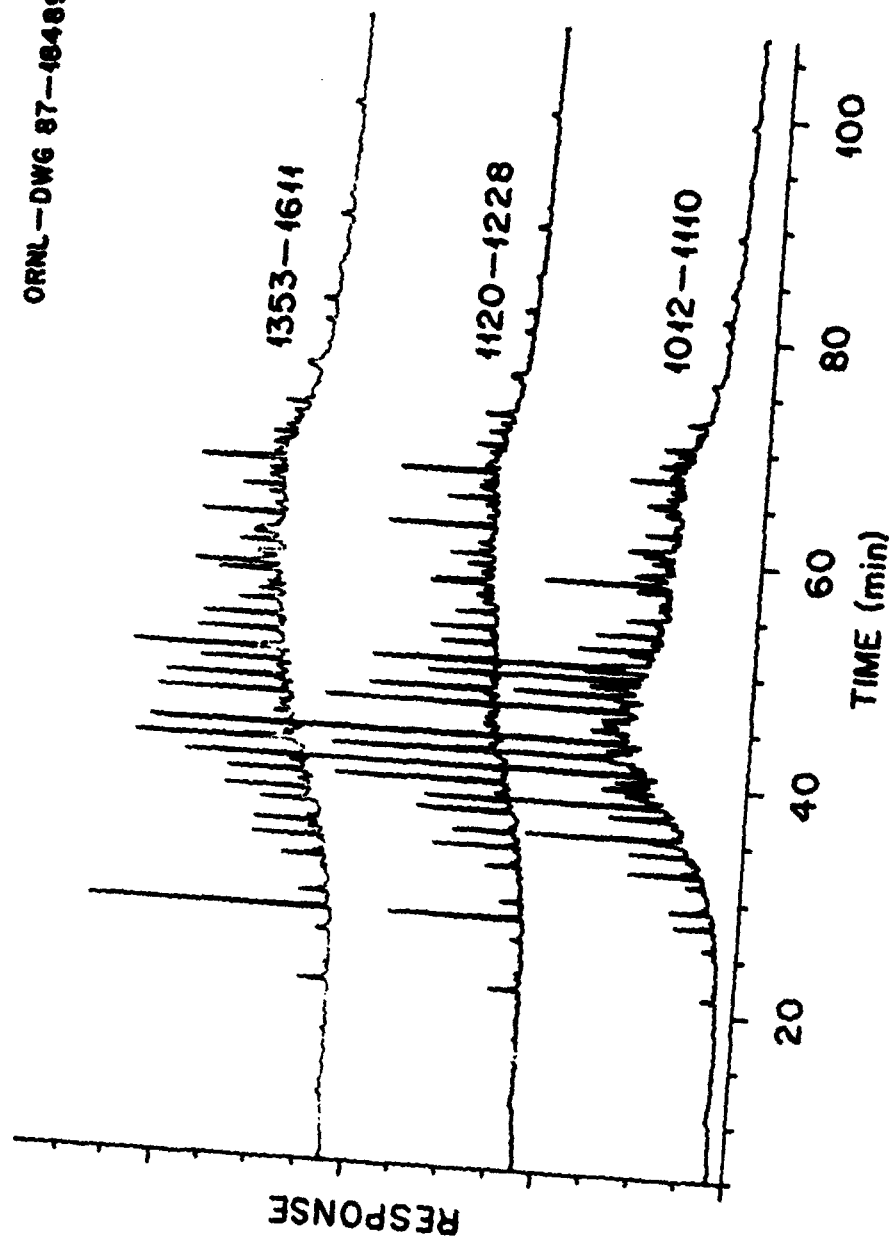


Figure 13. Comparison of the Chromatographable Major Organic Particulate Phase Organics in Time Resolved Samples at a Single Location in the DISCOM Motor Pool on September 24, 1986 (For GC conditions, see Figure 5)

**Table 16. Hourly Temporal Variations in Workplace Atmospheric Indicators at Single Locations in the DISCOM and Fourth Engineering Motor Pools**

Sampling Interval, Hrs	Indicators <sup>a</sup>			
	TSP, μg/m <sup>3</sup>	Benzene, μg/m <sup>3</sup> ,	n-C <sub>24</sub> , ng/m <sup>3</sup>	BaP, ng/m <sup>3</sup>
DISCOM <sup>b</sup> :				
0854-1000	190	NA	43	34
1021-1110	300	NA	46	- <sup>c</sup>
1120-1228	370	2.6	23	2.3
1241-1343	291	7.5	28	46
1353-1611	250	6.0	16	11
Overnight	70	NA	5.2	1.3
4th ENG. <sup>d</sup> :				
0859-1005	67	NA	28	1.2
1009-1109	61	NA	20	0.6
1110-1217	61	NA	5.9	0.2
1219-1319	37	NA	8.7	0.2
1323-1526	25	NA	41	0.1

<sup>a</sup>NA - not analyzed.

<sup>b</sup>DISCOM Middle, 9/24/86. DIS-24-TR-1 through -TR-5.

<sup>c</sup>Sample lost in fractionation.

<sup>d</sup>Engineering, North Wheel Bay 9/30/86, ENG-30-TR-1 through -TR-5.

general, these regulated contaminants were present at concentrations below the detection limits of the standard AEHA procedures. Most of the data for those regulated contaminants were reported as values less than the method detection limits. Consequently, a comparison of results between the two studies was not possible, except for CO and TSP.

As noted, the main exception was for CO. The 15 min average CO measurements in DISCOM ranged from 3.0 to 62.5 ppm, with both breathing zone and general area samples included. Our on-site measurements of 2 to 11 ppm with an Ecolyzer and Draeger tubes are consistent with those results. The CO readings were generally higher for DOL and Forth Engineers than for DISCOM, but none approached regulatory limits. The dust measurements had limits of detection of 200 to 1,100 μg/m<sup>3</sup>. Although they were not as sensitive as those for our much higher volume sampling, they were consistent with our measurements.

Table 17. Day-to-Day Temporal Variations in Workplace Atmospheric Contamination Indicators at Three Locations in the DISCOM Motor Pool

			Indicators <sup>a</sup>		
Location	Sampling		TSP, μg/m3	n-C <sub>24</sub> , ng/m <sup>3</sup>	BaP, ng/m <sup>3</sup>
	Date	Time			
MEZ					
	9/23	0819-1601	390	61	NA
		1223-1533	190	22	NA
	9/24	0843-1257	250	50	41
		1301-1541	250	22	18
	9/25	0822-1606	110	17	13
	9/26	0924-1508	170	31	-
MID					
	9/23	0823-1547	160	17	NA
	9/24	0855-1559	200	23	13
		1615-0816 <sup>b</sup>	70	5.2	1.3
	9/25	0840-1623	150	15	NA
		1626-0929 <sup>b</sup>	16	NA	NA
WST					
	9/23	0850-1600	190	16	NA
	9/24	0900-1621	290	24	7.9
	9/25	1151-1630	310	29	NA

<sup>a</sup>NA - not analyzed.

<sup>b</sup>Overnight 9/24-25 or 9/25-26.

The main conclusion from this brief comparison is that these regulated contaminants were present below regulatory levels in these workplace atmospheres. The larger air volumes collected for the unregulated constituents examined in this study allowed their measurement. A comparison of the two types of constituents would require the sampling and analysis of more contaminated workplace atmospheres or an increase in the sensitivities of the methods for determining the regulated constituents.

## CONCLUSIONS

This study has provided a detailed, side-by-side organic chemical characterization of diesel engine exhaust, ambient outside air, and the fuel/exhaust-contaminated workplace atmosphere to which military personnel are exposed the most frequently and at the highest levels. The main conclusions of this characterization are,

- (a) Diesel engine exhaust is very complex chemically. The concentrations of organic components are highly variable from engine to engine. The exhaust contains combustion-related components as well as uncombusted fuel and lubricants. It is likely that the differences in fuel composition accompanying a changeover of mobility fuel sources from petroleum to alternate or synthetic crude oils would result in changes in the composition of the engine exhaust.
- (b) Although diesel engine exhaust is a major contributor to the fuel-related contamination of the motor pool workplace atmosphere, it is not chemically identical to the motor pool garage workplace atmosphere and cannot serve as the sole surrogate for the toxicological study of the latter.
- (c) The motor pool garage workplace atmosphere contains many organic chemical components at concentrations considerably elevated above those in the outside ambient air. The organic chemical composition of the workplace atmosphere at different motor pools is qualitatively similar, but the contaminant concentrations may vary by factors of ca. 4 to 50-fold. The concentrations can vary by ca an order of magnitude as a function of time and location within a single motor pool. Such variations must be considered in designing bioassay conditions.
- (d) Settled dust from workplace surfaces and diesel exhaust particulates are not chemically identical to the suspended particulate matter in the motor pool atmospheres and cannot be used as surrogates for the latter. This may reflect chemical alteration processes and other sources such as ambient outside air.

- (e) Regulated air contaminants ( $\text{SO}_2$ , NO,  $\text{NO}_2$ , and TSP) were present below regulatory contamination levels and could not be determined by standard OSHA and ACGIH methodology. This prevented comparison with the unregulated constituents measured in this study.
- (f) Providing that a sufficient sample can be obtained, short-term air sampling (ca. 1 hr) is preferred to longer sampling periods (e.g., 3-8 hrs) because of the losses of particulate organic compounds, primarily alkanes below  $\text{C}_{24}$ , by sublimation during the latter.

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TABLE A-1. ABBREVIATIONS

AEHA	U.S. Army Environmental Hygiene Agency
AMP	4/68 Armored Brigade Motorpool
APC	Armored personnel carrier
BaP	Benzo[a]pyrene
Bn	Battalion
C <sub>x</sub>	Hydrocarbon or hydrocarbon group with x carbon atoms
CO <sub>2</sub>	Carbon dioxide
CTR	Center (sampling location)
DISCOM	Division Support Command
Div	Division
DOL	Directorate of Logistics
Dyna	Dynamometer test stand
E	East (side)
EMP	Forth Engineering Bn Motorpool
ERR	Data system error message (chromatographic peak out of range)
Exptl	Experimental
GM	General Motors
GOER	Ammunition carrying vehicle
GSD	Geometric Size Distribution
Hv	Heavy
IS	Internal standard for quantitation
m-	Meta isomer
MEZ	Mezzanine
MID	Middle (sampling location)
MMAD	Mass median aerodynamic diameter
MTR	Motor(pool)
n-	Normal isomer
NA	Not analyzed
NBS	National Bureau of Standards
NE	Northeast (side)
Nth	North
1-NPy	1-Nitropyrene
OSHA	Occupational Safety and Health Administration
p-	Para isomer
P	Compound is present but cannot be quantified
PAH	Polycyclic aromatic hydrocarbon
Pyrn	Pyrene
RPM	Engine revolutions per minute
SRM	Standard Reference Material
SW	Southwest (side)
TA	Time averaged (sample or sampling)
TR	Time resolved (sample or sampling)
TRK	Tracked vehicle (repair bay)
TSP	Total suspended particulates
TWA	Time weighted average
W	West (side)
WHL	Wheel vehicle (repair bay)
Wst	West (side)

TABLE A-2. PARTICULATE AND GASEOUS HYDROCARBON SAMPLING DATA  
FORT CARSON, COLORADO, SEPTEMBER 23 - OCTOBER 1, 1986

MOTORPOOL	DATE	SAMPLING PERIOD		SAMPLING LOCATION	SAMPLE NUMBER	PARTICLES, mg/filter	SAMPLING VOLUME, m3	PART. MATTER CONC., ug/m3	TOTAL C1-C6 HC, ppm	
		START	STOP							
DISCOM	09/23/86	09:07 AM	10:19 AM	MIDDLE	DIS-23-TR-1	36	147	245	4.8	
		10:31 AM	11:31 AM	MIDDLE	DIS-23-TR-2	32	142	225	4.9	
		11:40 AM	12:42 PM	MIDDLE	DIS-23-TR-3	16	147	109	5.1	
		12:55 PM	01:52 PM	CENTER	DIS-23-TR-4	24	135	178	4.3	
		01:59 PM	02:59 PM	CENTER	DIS-23-TR-5	27	142	190	6.4	
		03:08 PM	04:14 PM	MIDDLE	DIS-23-TR-6	27	157	172	7.1	
	09/24/86	08:19 AM	12:20 PM	MEZZANINE	DIS-23-TA-1	105	273	385	3.9	
		12:23 PM	03:33 PM	MEZZANINE	DIS-23-TA-2	59	312	169	6.6	
		08:32 AM	03:37 PM	MIDDLE	DIS-23-TA-3	123	791	155	5.5	
		08:50 AM	04:00 PM	WEST	DIS-23-TA-4	151	778	194		
		11:07 AM	11:12 AM	WEST	DIS-23-PAINT	223	10.6	21,038		
		08:54 AM	10:00 AM	MIDDLE	DIS-24-TR-1	30	157	191		
	09/24/86	10:12 AM	11:10 AM	MIDDLE	DIS-24-TR-2	42	138	304		
		11:20 AM	12:28 PM	MIDDLE	DIS-24-TR-3	60	162	370		
		12:41 PM	01:43 PM	MIDDLE	DIS-24-TR-4	43	148	291		
		01:53 PM	04:11 PM	MIDDLE	DIS-24-TR-5	82	328	250		
		08:43 AM	12:57 PM	MEZZANINE	DIS-24-TA-1	99	369	254	6	
		01:01 PM	03:41 PM	MEZZANINE	DIS-24-TA-2	61	245	249	3.5	
	09/24/86	08:55 AM	03:58 PM	MIDDLE	DIS-24-TA-3	152	772	197		
		09:00 AM	04:21 PM	WEST	DIS-24-TA-4	231	794	281		
		03:46 PM	08:16 AM	MEZZANINE	DIS-24-OVER-1	101	1485	68		
		04:15 PM	08:16 AM	MIDDLE	DIS-24-OVER-2	125	1778	70		

TABLE A-2. PARTICULATE AND GASEOUS HYDROCARBON SAMPLING DATA  
FORT CARSON, COLORADO, SEPTEMBER 23 - OCTOBER 1, 1986  
(Cont'd)

MOTORPOOL	DATE	SAMPLING PERIOD		SAMPLING LOCATION	SAMPLE NUMBER	PARTICLES, mg/filter	SAMPLING VOLUME, m3	PART. MATTER CONC., ug/m3	TOTAL C1-C6 HC, ppm
		START	STOP						
DISCOM	09/25/86	08:22 AM	04:06 PM	MEZZANINE	DIS-25-TA-1	84	780	108	
		08:40 AM	04:23 PM	MIDDLE	DIS-25-TA-2	127	868	146	
		11:51 AM	04:30 PM	WEST	DIS-25-TA-3	162	522	310	
		04:15 PM	09:22 AM	MEZZANINE	DIS-25-TA-OVER-1	52	1715	30	
		04:26 PM	09:29 AM	MIDDLE	DIS-25-TA-OVER-2	30	1913	16	
	09/26/86	08:24 AM	03:08 PM	MEZZANINE	DIS-26-TA-1	95	568	167	
		08:34 AM	03:11 PM	MIDDLE	DIS-26-TA-2	79	623	127	
		09:44 AM	03:19 PM	WEST	DIS-26-TA-3	118	606	195	
DOL	09/25/86	08:35 AM	03:44 PM	OUTSIDE	DOL-OUTSIDE BKGD	49	1021	48	
		03:33 PM	08:46 AM	LOWER LEVEL	DOL-25-TA-OVER-1	67	1863	34	
		03:29 PM	08:41 AM	UPPER LEVEL	DOL-25-TA-OVER-2	39	2611	15	
		06:42 AM	12:45 PM	TOP STORAGE	DOL-25-TA-1	35	918	38	
		12:47 PM	03:20 PM	UPPER LEVEL	DOL-25-TA-2	14	387	36	
		06:53 AM	03:31 PM	LOWER LEVEL	DOL-25-TA-3	110	1000	110	
	09/26/86	08:44 AM	03:48 PM	UPPER LEVEL	DOL-26-TA-1	21	996	21	
		08:48 AM	04:08 PM	LOWER LEVEL	DOL-26-TA-2	124	836	148	

TABLE A-2. PARTICULATE AND GASEOUS HYDROCARBON SAMPLING DATA  
FORT CARSON, COLORADO, SEPTEMBER 23 - OCTOBER 1, 1986  
(Cont'd)

MOTORPOOL	DATE	SAMPLING PERIOD		SAMPLING LOCATION	SAMPLE NUMBER	PARTICLES, mg/filter	SAMPLING VOLUME, m3	PART. MATTER CONC., ug/m3	TOTAL C1-C8 HC, ppm
		START	STOP						
4TH ENGR	09/29/86	04:26 PM	08:01 AM	WEST TRACK	ENG-28-TA-OVER-1	53	2478	21	
		04:21 PM	08:05 AM	NORTH WHEEL	ENG-28-TA-OVER-2	62	1746	36	
	09/30/86	08:58 AM	10:05 AM	NORTH WHEEL (N)	ENG-30-TR-1	12	180	67	
		10:09 AM	11:09 AM	NORTH WHEEL (N)	ENG-30-TR-2	10	163	61	
		11:10 AM	12:17 PM	NORTH WHEEL (N)	ENG-30-TR-3	11	181	61	
		12:19 PM	01:19 PM	NORTH WHEEL (N)	ENG-30-TR-4	6	162	37	
		01:23 PM	03:36 PM	NORTH WHEEL (N)	ENG-30-TR-5	9	358	25	
		09:14 AM	02:35 PM	WEST TRACK (SW)	ENG-30-TA-1	13	841	15	4.7
		09:19 AM	02:52 PM	WEST TRACK (NE)	ENG-30-TA-2	8	656	12	4.5
		08:45 AM	03:09 PM	NORTH WHEEL (E)	ENG-30-TA-3	23	635	36	
		08:53 AM	03:24 PM	NORTH WHEEL (W)	ENG-30-TA-4	11	612	18	
	10/01/86	08:58 AM	10:17 AM	NORTH WHEEL (N)	ENG-1-TR-1	28	213	131	
		10:36 AM	12:38 PM	NORTH WHEEL (N)	ENG-1-TR-2	32	329	97	
		12:51 PM	04:03 PM	NORTH WHEEL (N)	ENG-1-TR-3	68	518	131	
		09:06 AM	03:52 PM	WEST TRACK (SW)	ENG-1-TA-1	197	907	217	4.6
		09:07 AM	03:41 PM	WEST TRACK (NE)	ENG-1-TA-2	145	658	220	4.7
		08:54 AM	03:24 PM	NORTH WHEEL (E)	ENG-1-TA-3	105	647	162	
		08:56 AM	03:02 PM	NORTH WHEEL (W)	ENG-1-TA-4	104	673	155	

IR = Time Resolved Sample (ca. hourly)

TA = Time Averaged Sample (ca. 4, 8, or 16 hr average)

TABLE A-3. DRAEGER TUBE OR INSTRUMENTAL ANALYZER READINGS  
TAKEN DURING AIR SAMPLING AT DISCOM

Location	1986 Date	Time	Draeger Tube or Instrument	Reading <sup>a</sup> (ppm)
Center	9/23	1024	Ecolyzer CO	7
Mezzanine	9/23	0945	Draeger CO	2
			Draeger H <sub>2</sub> S	ND
			Draeger SO <sub>2</sub>	ND
			Draeger NO <sub>x</sub>	ND
Middle	9/23	1530	Draeger NO <sub>x</sub>	0.5
Mezzanine	9/24	1015	Draeger CO	5
			Draeger NO <sub>x</sub>	0.8
			Draeger NO <sub>2</sub>	0.2
			Draeger Hydrocarbons	ND
			Draeger H <sub>2</sub> S	ND
			Draeger SO <sub>2</sub>	ND
Middle	9/24	0845	Ecolyzer CO	11

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<sup>a</sup>ND - not detected



TABLE A-4. BIMODAL PARTICLE SIZE DISTRIBUTIONS  
FORT CARSON, COLORADO, AUGUST 23 - OCTOBER 1, 1986

<u>Motor Pool</u>	<u>Date</u>	<u>Particle Size, um MMAD</u>	
		<u>Small</u>	<u>Large</u>
DISCOM	09/23/86	0.46	3.2
		0.37	3.1
		0.86	4.0
		0.45	3.5
	09/24/86	0.43	3.2
		0.48	3.6
DOL	09/26/86	0.40	4.2
4th ENG	10/01/86	0.47	3.3

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MMAD - Mass Median Aerodynamic Diameter

TABLE A-5. DYNAMOMETER TEST FOR M-60 TANK ENGINE, PARTICULATE SAMPLE NO. 24 H-D-1

AFZC-D1-M ENGINE DYNAMOMETER TEST											
NOUN		MAKE	MODEL	S/N	JO#						
		M60A1			A4039		R 3681				
RUN NO	RUN TIME	RPM	MANIFOLD LEFT	PRESS RIGHT	HP	OIL PRESS	TIME IN	TIME OUT	TESTER	DATE	
1	10	750			50						
2	10	1000			100						
3	10	1100			125						
4											
5											
6											
7											
8											
9											
10											
LOW IDLE		HIGH IDLE		ACCELERATION		INSPECTOR					
REMARKS: (Continue on reverse side)											

TABLE A-6. DYNAMOMETER TEST REPORT FOR M-60 ENGINE EXHAUST SAMPLING (21-D-1)

ENGINE DYNAMOMETER TEST																	
AFZC-DI-M		MAKE		MODEL		S/N		JOB									
NOUN		MANIFOLD LEFT		PRESS RIGHT		HP		OIL PRESS		TIME IN		TIME OUT		TESTER		DATE	
RUN NO	RUN TIME	RPM															
1	05	750					50										
2	05	1000					100										
3	05	1100					125										
4	05	1300					150										
5	05	1500					200										
6	05	1700					250										
7	05	1700					350										
8	05	2200					525										
9	02	2400					680										
10	10	750					—										
LOW IDLE		HIGH IDLE		ACCELERATION		INSPECTOR											
REMARKS: (Continue on reverse side)																	

21-HV-D-1

for

TABLE A-7

MAJOR PARTICULATE ORGANIC COMPOUNDS AT DISCOM ON 9/23/86  
TIME RESOLVED SAMPLES

	Particle Concentration, ug/g		Air Concentration, ng/m3	
	907	1140	907	1140
Sampling Start:	907	1140	907	1140
Sampling End	1019	1242	1019	1242
Location:	MID	MID	MID	MID
Sample No.:	TR-1	TR-3	TR-1	TR-3
Component Name				
n-C14H30				
n-C15H32	0.5		0.1	
n-C16H34	21.8	44.6	5.3	4.9
n-C17H36	106.9	0.0	26.2	0.0
Pristane	21.4	0.0	5.2	0.0
n-C18H38	73.6	52.0	18.0	5.7
Phytane	62.9	0.0	15.4	0.0
n-C19H40	171.9	34.0	42.1	3.7
n-C20H42	173.0	51.6	42.4	5.6
n-C21H44 + Pym	431.7	114.5	105.7	12.5
n-C22H46	292.9	122.1	71.7	13.3
n-C23H48	189.5	147.6	46.4	16.1
n-C24H50	118.6	183.8	29.0	20.0
n-C25H52	82.1	89.1	20.1	9.7
n-C26H54	49.4	105.2	12.1	11.5
n-C27H56	62.8	163.1	15.4	17.8
n-C28H58	40.6	26.2	9.9	2.8
n-C29H60	77.6	156.1	19.0	17.0
n-C30H62	55.3	101.4	13.5	11.0
n-C31H64	94.9	210.0	23.2	22.9
n-C32H66	48.5	62.5	11.9	6.8
n-C33H68	50.0	96.6	12.3	10.5
n-C34H70	13.9	0.0	3.4	0.0
n-C35H72	70.3	0.0	17.2	0.0
n-C36H74	0.0	0.0	0.0	0.0

TABLE A-8. MAJOR PARTICULATE ORGANIC COMPOUNDS IN DISCOM ON 9/23/86  
TIME AVERAGED SAMPLES

Sampling Start: Sampling End: Location: Sample No.: Component Name	Particle Concentration, ug/g				Air Concentration, ng/m <sup>3</sup>			
	819	1223	823	850	819	1223	823	850
	1601 MEZ TA-1	1533 MEZ TA-2	1547 MID TA-3	1600 WEST TA-4	1601 MEZ TA-1	1533 MEZ TA-2	1547 MID TA-3	1600 WEST TA-4
n-C14H30	0.0	0.0			0.0	0.0		
n-C15H32	0.0	0.0		0.0	0.0	0.0		0.0
n-C16H34	2.1	0.0	14.9	0.0	0.8	0.0	2.3	0.0
n-C17H36	26.0	0.0	0.0	14.1	10.0	0.0	0.0	2.7
Pristane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
n-C18H38	11.8	9.4	0.0	27.7	4.6	1.8	0.0	5.4
Phytane	0.0	0.0	0.0	10.9	0.0	0.0	0.0	2.1
n-C19H40	12.9	15.1	15.0	19.5	5.0	2.8	2.3	3.8
n-C20H42	37.9	41.1	17.9	17.2	14.6	7.8	2.8	3.3
n-C21H44 + Pyn	212.3	83.1	60.1	52.4	81.7	15.7	9.3	10.2
n-C22H46	360.8	117.5	71.9	61.4	138.8	22.2	11.2	11.9
n-C23H48	300.4	140.7	98.4	80.0	115.5	26.6	15.3	15.5
n-C24H50	157.9	116.3	106.6	79.7	60.7	22.0	16.6	15.5
n-C25H52	88.2	74.9	65.2	70.8	33.9	14.2	10.1	13.7
n-C26H54	114.4	41.7	64.9	47.7	44.0	7.9	10.1	9.3
n-C27H56	38.9	76.3	60.5	80.6	14.9	14.4	9.4	15.6
n-C28H58	14.8	4.3	32.5	56.2	5.7	0.8	5.0	10.9
n-C29H60	44.1	94.1	59.7	90.6	17.0	17.8	9.3	17.6
n-C30H62	26.7	71.7	49.5	60.4	10.3	13.6	7.7	11.7
n-C31H64	70.5	126.5	117.5	161.3	27.1	23.9	18.3	31.3
n-C32H66	33.1	38.8	41.6	50.1	12.7	7.3	6.5	9.7
n-C33H68	36.8	61.0	56.0	66.4	14.2	11.5	8.7	12.9
n-C34H70	0.0	0.0	0.0	15.8	0.0	0.0	0.0	3.1
n-C35H72	0.0	34.1	19.5	0.0	0.0	6.4	3.0	0.0
n-C36H74	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

TABLE A-9. SELECTED VOLATILE ORGANIC COMPOUNDS AT DISCOM  
ON 9/23/86. TR SAMPLES

	Concentration, ug/m <sup>3</sup>					
Sampling Start:	907	1031	1140	1255	1359	1508
Sampling End:	1019	1131	1242	1352	1459	1614
Location:	MID	MID	MID	CTR	CTR	MID
Sample No.:	TR-1	TR-2	TR-3	TR-4	TR-5	TR-6
<u>Component</u>	<u>          </u>	<u>          </u>	<u>          </u>	<u>          </u>	<u>          </u>	<u>          </u>
Hexane	21	6.2	9.3	11	10	I
Benzene	10	3.1	2.5	4.7	3.1	0.8
Heptane	19	8.6	4.6	8.5	8.1	36
Toluene	73	46	22	19	16.7	40
Octane	11	6.7	2.2	1	2.8	4.9
Ethyl Benzene	14	159	43	18	20	30
m/p-xylenes	50	461	202	75	101	164

I - interference prevented quantitation

TABLE A-10. MAJOR PARTICULATE ORGANIC COMPOUNDS IN DISCON ON 9/24/86  
TIME RESOLVED SAMPLES

Sampling Start: Sampling End: Location: Sample No.: Component Name	Particle Concentration, ug/s						Air Concentration, ng/m3					
	854	1012	1120	1241	1353	854	854	1012	1120	1241	1353	854
	1000	1110	1228	1343	1611	1611	1000	1110	1228	1343	1611	1611
	MID	MID	MID	MID	MID	MID	MID	MID	MID	MID	MID	MID
	TR-1	TR-2	TR-3	TR-4	TR-5	TMA	TR-1	TR-2	TR-3	TR-4	TR-5	TMA
n-C14H30	8.4							2.5				
n-C15H32	0.0							0.0				
n-C16H34	5.7	21.7	15.1	29.6	15.2	16.8	1.1	6.6	5.6	9.6	3.6	4.8
n-C17H36	131.7	71.4	35.7	70.9	34.0	62.1	25.2	21.7	13.2	26.6	8.5	18.0
Pristane	44.2	17.9	10.7	19.2	10.2	16.6	8.5	5.4	4.0	5.6	2.6	4.7
n-C18H38	142.1	69.7	30.6	56.4	23.5	56.6	27.1	21.2	11.4	16.4	5.9	14.4
Phytane	145.3	77.0	29.4	57.6	26.3	59.4	27.8	23.4	10.9	16.7	6.6	15.0
n-C19H40	443.6	141.7	57.0	130.0	39.5	140.1	84.8	43.1	21.1	37.6	9.9	23.6
n-C20H42	399.4	217.2	69.0	143.7	48.3	151.2	76.3	66.1	25.6	41.7	12.1	37.9
n-C21H44 + Pym	536.7	601.6	111.3	355.0	100.4	290.7	102.9	183.1	41.2	103.1	25.1	76.6
n-C22H46	676.1	547.2	124.9	317.4	89.9	288.5	129.2	166.6	46.3	82.2	22.5	77.0
n-C23H48	353.9	370.1	87.1	159.3	101.2	190.4	87.6	112.6	32.3	46.3	25.3	49.9
n-C24H50	225.3	152.5	62.3	97.2	63.3	109.0	43.0	46.4	23.1	29.2	15.6	29.2
n-C25H52	125.6	88.9	54.9	47.9	53.5	70.3	24.0	27.0	20.3	13.9	13.4	18.5
n-C26H54	84.6	86.9	55.8	53.6	18.8	51.9	16.2	26.4	20.7	15.6	4.7	14.3
n-C27H56	90.9	38.7	64.4	69.9	51.3	61.3	17.4	11.8	23.6	20.3	12.8	16.5
n-C28H58	41.0	19.2	24.9	28.4	30.0	29.1	7.8	5.8	8.2	6.3	7.5	7.7
n-C29H60	104.7	46.3	110.5	62.3	61.1	75.0	20.0	14.1	40.9	18.1	15.3	20.8
n-C30H62	0.0	43.2	56.3	28.6	35.6	33.2	0.0	13.1	20.9	8.3	8.9	10.0
n-C31H64	138.6	51.3	122.2	66.7	59.9	84.0	26.5	15.6	45.3	20.0	15.0	23.0
n-C32H66	49.2	31.2	33.3	23.7	31.3	33.5	9.4	9.5	12.4	6.9	7.8	9.0
n-C33H68	73.5	23.4	32.6	36.0	21.7	34.9	14.0	7.1	12.1	10.5	5.4	9.1
n-C34H70	0.0		15.3		13.0		0.0		5.7		3.3	
n-C35H72	180.8		4.7				34.5		1.7			
n-C36H74	0.0						0.0					

TABLE A-11. MAJOR PARTICULATE ORGANIC COMPOUNDS IN DISCOM ON 9/24/86  
TIME AVERAGED SAMPLES

	Particle Concentration, ug/g				Air Concentration, ng/m3			
	*****				*****			
Sampling Start:	843	1303	855	900	843	1303	855	900
Sampling End:	1257	1541	1559	1621	1257	1541	1559	1621
Location:	ME2	ME2	MID	WEST	ME2	ME2	MID	WEST
Sample No.:	TA-1	TA-2	TA-3	TA-4	TA-1	TA-2	TA-3	TA-4
Component Name	-----				-----			
n-C14H30	0.0		0.0	0.0	0.0		0.0	0.0
n-C15H32	0.0		0.0	0.0	0.0		0.0	0.0
n-C16H34	0.0	17.9	3.8	2.9	0.0	4.5	0.8	0.8
n-C17H36	32.8	26.4	24.9	14.2	8.3	6.6	4.9	4.1
Pristane	9.6	9.9	6.2	3.9	2.4	2.5	1.2	1.1
n-C18H38	32.1	22.9	14.1	11.5	8.2	5.7	2.8	3.3
Phytane	0.0	28.4	24.1	11.7	0.0	7.1	4.7	3.4
n-C19H40	41.8	57.6	29.1	18.5	10.6	14.4	5.7	5.4
n-C20H42	104.6	100.4	51.0	25.6	26.6	25.0	10.0	7.4
n-C21H44 + Pym	783.9	236.0	151.1	70.4	179.2	58.7	29.7	20.5
n-C22H46	959.8	225.5	189.5	71.2	244.3	56.1	37.3	20.7
n-C23H48	518.6	177.6	134.2	74.9	132.0	44.2	26.4	21.8
n-C24H50	195.4	89.8	119.1	83.3	49.7	22.4	23.4	24.2
n-C25H52	163.7	108.0	84.2	60.6	41.7	26.9	16.6	17.6
n-C26H54	141.8	80.2	88.2	53.6	36.1	20.0	17.4	15.6
n-C27H56	80.8	72.9	61.6	45.8	20.6	18.1	12.1	13.3
n-C28H58	30.7	59.5	42.0	0.0	7.8	14.8	8.3	0.0
n-C29H60	91.7	107.3	99.3	88.6	23.3	26.7	19.6	25.8
n-C30H62	55.6	60.9	49.5	43.0	14.2	15.2	9.8	12.5
n-C31H64	146.5	114.0	128.3	115.0	37.3	28.4	25.3	33.5
n-C32H66	68.9	60.3	46.8	44.4	17.5	15.0	9.2	12.9
n-C33H68	76.6	59.1	43.8	67.6	19.5	14.7	8.6	19.7
n-C34H70		36.2	22.1	15.8		9.0	4.4	4.6
n-C35H72		12.5	0.0	25.4		3.1	0.0	7.4
n-C36H74		9.7	2.8	16.6		2.4	0.5	4.8



Table A-12. Particulate 4 to 6-Ring Polycyclic Aromatic Hydrocarbon Dermal Tumorigens at DISCOM on 9/24/86

		Air Concentration, ng/m3									
Sampling Start:		854	1120	1241	1353	843	1301	855	900	854	
Sampling End:		1000	1228	1343	1611	1257	1541	1559	1621	1611	
Location:		MID	MID	MID	MID	MEZ	MEZ	MID	WEST	MID	
Sample No.:	PAH	TR-1	TR-3	TR-4	TR-5	TA-1	TA-2	TA-3	TA-4	TWA	
Benz(a)anthracene		26	2	41	7	37	11	13	7	16	
Chrysene		44	4	60	13	48	18	20	12	26	
Benzo(b/j)fluoranthenes		34	2	36	9	55	17	27	4	17	
Benzo(k)fluoranthene		9	1	0	4	10	8	6	9	4	
Benzo(a)fluoranthene		11	1	14	3	12	4	5	3	6	
Benzo(e)pyrene		24	2	29	8	18	13	9	66	14	
Benzo(a)pyrene		34	2	46	11	41	18	13	8	20	
Dibenz(a,j)anthracene		5	0	6	1	7	2	3	41	3	
Indeno(123-cd)pyrene		69	3	71	16	31	28	14	456	34	
Dibenz(a,c/a,h)anthracenes		4	0	4	2	5	2	1	37	2	
Benzo(ghi)perylene		87	3	0	20	74	33	32	573	26	

		Particle Concentration, ug/g									
Benz(a)anthracene		139	4	101	30	146	44	68	24	59	
Chrysene		231	10	208	51	190	74	100	41	107	
Benzo(b/j)fluoranthenes		177	6	124	34	217	69	136	15	73	
Benzo(k)fluoranthene		49	4	0	18	39	31	28	30	18	
Benzo(a)fluoranthene		56	2	48	11	49	17	24	9	25	
Benzo(e)pyrene		124	5	98	32	72	53	48	226	57	
Benzo(a)pyrene		177	6	158	42	163	71	65	27	83	
Dibenz(a,j)anthracene		27	1	19	6	26	7	16	142	11	
Indeno(123-cd)pyrene		359	7	246	64	123	112	70	1,568	144	
Dibenz(a,c/a,h)anthracenes		20	1	15	7	21	9	5	126	10	
Benzo(ghi)perylene		453	9	0	78	293	133	162	1,971	124	

TABLE A-13. SELECTED VOLATILE ORGANICS AT DISCOM ON 9/24/86  
TR SAMPLES

	Concentration, ug/m <sup>3</sup>			
Sampling Start:	1120	1241	1353	1120
Sampling End:	1228	1343	1611	1611
Location:	MID	MID	MID	MID
Sample No.:	TR-3	TR-4	TR-5	TWA
<u>Component</u>	<u>      </u>	<u>      </u>	<u>      </u>	<u>      </u>
Hexane	7.2	9.6	18	13
Benzene	2.6	7.5	6.0	6.0
Heptane	5.6	5.3	14	9.9
Toluene	16	23	51	36
Octane	2.7	2.0	5.6	4.1
Ethyl Benzene	6.0	9.0	11	9.3
m/p-xylenes	14	32	116	71

TABLE A-14. MAJOR PARTICULATE ORGANIC COMPOUNDS AND 4- TO 6-RING  
PAH DERMAL TUMORIGENS IN OVERNIGHT AIR SAMPLE AT DISCOM  
(DIS-24-TA-OVER2)

Component Name	Mass/Filter ug/filter	Part. Conc. ug/g	Air Conc. ng/m3
n-C14H30		0.0	0.0
n-C15H32	0.76	6.1	0.4
n-C16H34	2.45	19.6	1.4
n-C17H36	6.38	51.0	3.6
Pristane	1.88	15.0	1.1
n-C18H38	2.62	21.0	1.5
Phytane	3.69	29.5	2.1
n-C19H40	3.91	31.3	2.2
n-C20H42	4.56	37.3	2.6
n-C21H44 + Pyr n	11.67	93.4	6.6
n-C22H46	6.17	49.4	3.5
n-C23H48	10.83	86.7	6.1
n-C24H50	9.20	73.6	5.2
n-C25H52	9.94	79.5	5.6
n-C26H54	4.23	33.9	2.4
n-C27H56	13.12	104.9	7.4
n-C28H58	5.65	45.2	3.2
n-C29H60	18.82	150.5	10.6
n-C30H62	8.72	69.7	4.9
n-C31H64	41.00	328.0	23.1
n-C32H66	9.22	73.7	5.2
n-C33H68	16.71	133.7	9.4
n-C34H70	1.48	11.8	0.8
n-C35H72	2.05	16.4	1.2
n-C36H74		0.0	0
Benz(a)anthracene		7.3	0.5
Chrysene		17.0	1.1
Benzo(b/j)fluoranthenes		28.0	2.0
Benzo(k)fluoranthene		11.0	0.8
Benzo(a)fluoranthene		4.3	0.3
Benzo(a)pyrene		23.0	1.6
Benzo(a)pyrene		19.0	1.3
Dibenz(a,j)anthracene		3.7	0.3
Indeno(1,2,3-cd)pyrene		50.0	3.5
Dibenz(a,c/a,h)anthracenes		4.1	0.3
Benzo(ghi)perylene		62.0	4.4

TABLE A-15. MAJOR PARTICULATE ORGANIC COMPOUNDS IN DISCON ON 9/25/86  
TIME AVERAGED SAMPLES

	Particle Concentration, ug/g			Air Concentration, ng/m3		
	*****			*****		
Sampling Start:	822	840	1151	822	840	1151
Sampling End:	1606	1623	1630	1606	1623	1630
Location:	MEZ	MID	WEST	MEZ	MID	WEST
Sample No.:	TA-1	TA-2	TA-3	TA-1	TA-2	TA-3
Component Name	-----			-----		
n-C14H30	0.0	0.0	0.0	0.0	0.0	0.0
n-C15H32	0.0	2.0	0.0	0.0	0.3	0.0
n-C16H34	30.1	15.0	3.2	3.2	2.2	1.0
n-C17H36	40.3	161.0	48.6	4.3	23.8	15.1
Pristane	0.0	22.6	7.3	0.0	3.3	2.3
n-C18H38	13.3	74.6	23.7	1.4	11.0	7.4
Phytane	7.4	51.9	17.7	0.8	7.7	5.5
n-C19H40	19.1	95.6	57.0	2.1	14.1	17.7
n-C20H42	34.2	116.4	59.8	3.7	17.2	18.6
n-C21H44 + Pyrn	74.2	130.2	100.7	8.0	19.2	31.3
n-C22H46	120.4	134.0	83.9	13.0	19.8	26.0
n-C23H48	111.6	127.8	63.5	12.0	18.9	19.7
n-C24H50	157.4	103.7	91.7	16.9	15.3	28.5
n-C25H52	136.7	71.9	47.9	14.7	10.6	14.9
n-C26H54	90.8	43.9	51.9	9.8	6.5	16.1
n-C27H56	329.7	198.9	70.8	35.5	29.4	22.0
n-C28H58	116.3	66.2	49.5	12.5	9.8	15.4
n-C29H60	388.9	223.2	101.1	41.9	33.0	31.4
n-C30H62	171.4	93.8	60.9	18.5	13.8	18.9
n-C31H64	1,243.6	569.9	197.8	133.9	84.2	61.4
n-C32H66	224.1	108.4	57.1	24.1	16.0	17.7
n-C33H68	578.4	243.0	81.7	62.3	35.9	25.4
n-C34H70	75.3	16.7	41.7	8.1	2.5	12.9
n-C35H72	22.4	17.0	15.6	2.4	2.5	4.8
n-C36H74		0.0	14.4		0.0	4.5

TABLE A-16. MAJOR PARTICULATE ORGANIC COMPOUNDS AT DISCOM  
MEZ ON 9/26/86, TIME AVERAGED SAMPLE, 924-1508 Hrs.

Component Name	Part. Conc. ug/g	Air Conc. ng/m3
n-C14H30		
n-C15H32	15.0	2.5
n-C16H34	14.0	2.3
n-C17H36	57.2	9.6
Pristane	16.2	2.7
n-C18H38	30.2	5.1
Phytane	34.5	5.8
n-C19H40	70.2	11.7
n-C20H42	85.5	14.3
n-C21H44 + Pyrn	347.7	58.2
n-C22H46	150.9	25.2
n-C23H48	281.4	47.1
n-C24H50	187.8	31.4
n-C25H52	113.8	19.0
n-C26H54	56.5	9.5
n-C27H56	60.5	10.1
n-C28H58	60.0	10.0
n-C29H60	67.1	11.2
n-C30H62	55.2	9.2
n-C31H64	146.1	24.4
n-C32H66	35.6	5.9
n-C33H68	67.2	11.2
n-C34H70	12.4	2.1
n-C35H72	21.0	3.5
n-C36H74		

TABLE A-17. MAJOR PARTICULATE ORGANIC COMPOUNDS AND 4- TO 6-RING  
PAH DERMAL TUMORIGENS IN DISCOM DUST SAMPLE

Component Name	Mass/Sample ug/sample	Part. Conc. ug/g
n-C14H30		
n-C15H32		
n-C16H34		0.0
n-C17H36	1.09	9.9
Pristane		0.0
n-C18H38	0.72	6.5
Phytane		0.0
n-C19H40	1.34	12.2
n-C20H42	0.71	6.4
n-C21H44 + Pyn	1.52	13.8
n-C22H46	1.49	13.5
n-C23H48		0.0
n-C24H50	4.19	38.1
n-C25H52	1.72	15.7
n-C26H54	2.11	19.2
n-C27H56	2.14	19.4
n-C28H58	1.25	11.4
n-C29H60	2.32	21.1
n-C30H62	2.04	18.5
n-C31H64	0.84	7.7
n-C32H66	0.97	8.8
n-C33H68	1.23	11.2
n-C34H70		
n-C35H72		
n-C36H74		
Benz(a)anthracene		0.5
Chrysene		2.1
Benzo(b/j)fluoranthenes		2.2
Benzo(k)fluoranthene		0.7
Benzo(a)fluoranthene		0.3
Benzo(e)pyrene		1.2
Benzo(a)pyrene		0.7
Dibenz(a,j)anthracene		0.3
Indeno(1,2,3-cd)pyrene		1.6
Dibenz(a,c/a,h)anthracenes		0.3
Benzo(ghi)perylene		1.6

TABLE A-16. MAJOR PARTICULATE ORGANIC COMPOUNDS AT FORTH ENGINEERING BN MOTOR POOL ON 9/30/86  
TIME RESOLVED SAMPLES AT NORTH END OF NORTH WHEEL BAY

Sampling Start: Sampling End: Sample No.: Component Name	Particle Concentration, ug/g					Air Concentration, ng/m <sup>3</sup>				
	859	1009	1110	1219	1323	859	1009	1110	1219	1323
n-C14H30	24.5					1.6				
n-C15H32	115.0	76.5		304.0	164.5	7.7	4.7		11.3	4.1
n-C16H34	299.2	429.9	405.5	362.9	219.4	19.9	26.4	24.6	13.4	5.5
n-C17H36	39.6	71.7	0.0	0.0	0.0	2.6	4.4	0.0	0.0	0.0
Pristane	150.0	160.3	124.5	255.1	168.4	10.0	9.8	7.6	9.4	4.2
n-C18H38	126.7	125.7	0.0	350.9	95.7	8.4	7.7	0.0	13.0	2.4
Phytane	249.2	248.5	199.1	532.1	131.1	16.6	15.2	12.1	19.7	3.3
n-C19H40	424.2	309.4	400.0	452.0	186.8	28.3	19.0	24.3	16.7	4.7
n-C20H42	875.0	713.7	420.0	1,741.9	452.7	58.3	43.8	25.5	64.5	11.4
n-C21H44 + Pym	491.7	297.9	139.1	514.2	235.4	32.8	18.3	8.5	19.0	5.9
n-C22H46	413.3	327.6	67.3	271.5	168.7	27.6	20.1	4.1	10.1	4.2
n-C23H48	425.0	317.7	96.4	233.9	164.3	28.3	19.5	5.9	8.7	4.1
n-C24H50	145.0	132.8	62.7	122.1	58.2	9.7	8.1	3.8	4.5	1.5
n-C25H52	87.5	119.2	0.0	130.1	0.0	5.8	7.3	0.0	4.8	0.0
n-C26H54	216.7	291.4	83.6	191.6	190.7	14.4	17.9	5.1	7.1	4.8
n-C27H56	52.5	107.6	19.1	0.0	ERR	3.5	6.6	1.2	0.0	ERR
n-C28H58	184.2	340.6	107.3	180.2	116.3	12.9	20.9	6.5	6.7	2.9
n-C29H60	85.0	154.7	0.0	181.3	46.5	5.7	9.5	0.0	6.7	1.2
n-C30H62	294.2	706.3	201.8	263.5	17.4	19.6	43.3	12.3	9.8	0.4
n-C31H64	92.5	141.7		0.0		6.2	8.7		0.0	
n-C32H66	167.5	262.4		127.6		11.2	16.1		4.7	
n-C33H68		0.0					0.0			
n-C34H70		0.0					0.0			
n-C35H72		74.3					4.6			
n-C36H74										

TABLE A-19. MAJOR PARTICULATE ORGANIC COMPOUNDS AT FORTH ENGINEERING BN  
MOTOR POOL ON 9/30/86, TIME AVERAGED SAMPLES

	Particle Concentration, ug/g			Air Concentration, ng/m3		
	*****			*****		
Sampling Start:	914	919	853	914	919	853
Sampling End:	1435	1452	1523	1435	1452	1523
Location:	W Trk*	W Trk+	N Whl**	W Trk*	W Trk+	N Whl**
Sample No.:	TA-1	TA-2	TA-4	TA-1	TA-2	TA-4
Component Name	-----			-----		
n-C14H30						
n-C15H32	33.3			0.5		
n-C16H34	39.9	92.3		0.6	1.1	
n-C17H36	224.5	252.9	730.0	3.5	3.1	13.1
Pristane	46.9	39.0	30.9	0.7	0.5	0.6
n-C18H38	117.8	176.8	104.8	1.8	2.2	1.9
Phytane	64.2	0.0	78.8	1.0	0.0	1.4
n-C19H40	122.9	211.5	130.3	1.9	2.6	2.3
n-C20H42	230.0	247.7	182.9	3.6	3.0	3.3
n-C21H44	350.9	693.4	537.4	5.4	8.5	9.7
n-C22H46	179.4	364.2	308.6	2.8	4.4	5.5
n-C23H48	241.1	362.7	366.8	3.7	4.4	6.6
n-C24H50	272.9	468.4	452.1	4.2	5.7	8.1
n-C25H52	142.3	301.5	151.3	2.2	3.7	2.7
n-C26H54	80.9	166.2	100.8	1.3	2.0	1.8
n-C27H56	168.1	244.6	231.1	2.6	3.0	4.2
n-C28H58	47.5	47.8	86.5	0.7	0.6	1.6
n-C29H60	146.6	180.0	290.7	2.3	2.2	5.2
n-C30H62	57.9	91.8	141.6	0.9	1.1	2.5
n-C31H64	186.9	414.5	541.2	2.9	5.1	9.7
n-C32H66	35.9	0.0	142.2	0.6	0.0	2.6
n-C33H68	49.3	21.7	228.5	0.8	0.3	4.1
n-C34H70						
n-C35H72						
n-C36H74						

\* SW corner

+ NE corner

\*\* W corner



TABLE A-20. 4- TO 6-RING PAH DERMAL TUMORIGENS AT THE FORTH ENGINEERING  
BN MOTOR POOL ON 9/30/86, TIME RESOLVED SAMPLES

Air Concentration, ng/m3					
*****					
Sampling Start:	859	1009	1110	1219	1323
Sampling End:	1005	1109	1217	1319	1536
Location:	Nth Whl	Nth Whl	Nth Whl	Nth Whl	Nth Whl
Sample No.:	TR-1	TR-2	TR-3	TR-4	TR-5
PAH					
*****					
Benz(a)anthracene	0.8	0.3	0.1	0.2	0.9
Chrysene	1.9	0.9	0.6	0.6	0.3
Benzo(b,j)fluoranthenes	1.2	0.8	0.4	0.5	0.1
Benzo(k)fluoranthene	0.6	0.4	0.2	0.3	0.1
Benzo(a)fluoranthene	0.4	0.2	0.2	0.2	0.1
Benzo(e)pyrene	1.2	0.7	0.4	0.3	0.1
Benzo(a)pyrene	1.2	0.6	0.2	0.2	0.1
Dibenz(a,j)anthracene	0.4	0.2	0.1	0.1	0.0
Indeno(123-cd)pyrene	2.2	1.5	0.5	0.6	0.2
Dibenz(a,c/a,h)anthracenes	0.2	0.2	0.1	0.2	0.0
Benzo(ghi)perylene	4.6	2.5	0.7	0.7	0.3
Particle Concentration, ug/g					
-----					
Benz(a)anthracene	12.5	5.5	2.3	4.2	34.4
Chrysene	29.2	15.0	9.1	16.7	10.3
Benzo(b,j)fluoranthenes	17.5	13.0	6.0	14.0	5.7
Benzo(k)fluoranthene	8.3	6.6	3.5	8.2	2.9
Benzo(a)fluoranthene	5.6	3.8	3.1	6.0	3.1
Benzo(e)pyrene	17.5	12.0	6.0	7.0	4.3
Benzo(a)pyrene	17.5	10.0	2.8	5.3	2.7
Dibenz(a,j)anthracene	5.3	3.0	2.5	2.7	1.2
Indeno(123-cd)pyrene	33.3	24.0	8.6	15.7	6.7
Dibenz(a,c/a,h)anthracenes	3.5	3.2	2.0	6.7	1.7
Benzo(ghi)perylene	68.3	41.0	11.8	20.0	10.3

TABLE A-21. MAJOR PARTICULATE ORGANIC COMPOUNDS AND 4- TO 6-RING PAH DERIVAT TUMORIGENS IN DOL ON 9/25/86, DOL-25-TA-3

Component Name	Part. Conc. ug/g	Air Conc. ng/m3
n-C14H30		
n-C15H32	1.0	0.1
n-C16H34	7.9	0.9
n-C17H36	16.0	1.8
Pristane	4.5	0.5
n-C18H38	13.4	1.5
Phytane	16.3	1.8
n-C19H40	15.8	1.7
n-C20H42	34.0	3.7
n-C21H44 + Pyrn	99.1	10.9
n-C22H46	44.6	4.9
n-C23H48	78.6	8.6
n-C24H50	66.9	7.4
n-C25H52	53.5	5.9
n-C26H54	33.0	3.6
n-C27H56	45.0	4.9
n-C28H58	23.1	2.5
n-C29H60	78.3	8.6
n-C30H62	46.4	5.1
n-C31H64	131.0	14.4
n-C32H66	31.9	3.5
n-C33H68	57.3	6.3
n-C34H70	7.2	0.8
n-C35H72	16.1	1.8
n-C36H74	9.8	1.1
Benz(a)anthracene	9.1	1.0
Chrysene	18.3	2.0
Benzo(b/j)fluoranthenes	30.9	3.4
Benzo(k)fluoranthene	12.3	1.3
Benzo(a)fluornathene	5.2	0.6
Benzo(e)pyrene	34.1	3.7
Benzo(a)pyrene	29.2	3.2
Dibenz(a,j)anthracene	3.6	0.4
Indeno(1,2,3-cd)pyrene	65.4	7.2
Dibenz(a,c/a,h)anthracenes	3.2	0.4
Benzo(ghi)perylene	145.0	16.0

TABLE A-22. MAJOR PARTICULATE ORGANIC COMPOUNDS AT 4- TO 6-RING  
PAH DERMAL TUMORIGENS IN AMBIENT OUTSIDE AIR SAMPLE  
(DOL-OUTSIDE BACKGROUND)

Component Name	Mass/Filter ug/filter	Part. Conc. ug/g	Air Conc. ng/m3
n-C14H30			
n-C15H32			
n-C16H34			
2-MeC16H34	0.93	19.0	0.9
n-C17H36		0.0	0.0
Pristane		0.0	0.0
n-C18H38	0.85	17.4	0.8
Phytane		0.0	0.0
n-C19H40	0.39	8.0	0.4
n-C20H42	1.32	26.8	1.3
n-C21H44 + Pyrn	4.71	96.2	4.6
n-C22H46	3.71	75.8	3.6
n-C23H48	5.01	102.3	4.9
n-C24H50	3.48	71.1	3.4
n-C25H52	2.68	54.6	2.6
n-C26H54	1.04	21.3	1.0
n-C27H56	1.42	29.1	1.4
n-C28H58	Invalid	ERR	ERR
n-C29H60	2.09	42.7	2.0
n-C30H62	1.53	31.1	1.5
n-C31H64	1.37	28.0	1.3
n-C32H66	0.69	14.0	0.7
n-C33H68	2.70	55.0	2.6
n-C34H70	0.68	13.9	0.7
n-C35H72			
n-C36H74			
Benz(a)anthracene		4.9	0.2
Chrysene		11.5	0.5
Benzo(b,j)fluoranthenes		9.3	0.4
Benzo(k)fluoranthene		6.4	0.3
Benzo(a)fluoranthene		2.9	0.1
Benzo(e)pyrene		9.4	0.5
Benzo(a)pyrene		8.0	0.4
Dibenz(a,j)anthracene		3.7	0.2
Indeno(1,2,3-cd)pyrene		17.0	0.8
Dibenz(a,c/a,h)anthracenes		3.0	0.1
Benzo(ghi)perylene		21.8	1.1

TABLE A-23. MAJOR PARTICULATE ORGANIC COMPOUNDS AND 4- TO 6-RING PAH DERMAL TUMORIGENS IN BLANK FILTER

Component Name	Mass/Filter ug/filter
-----	-----
n-C14H30	
n-C15H32	
n-C16H34	0.37
n-C17H36	
Pristane	
n-C18H38	0.41
Phytane	1.06
n-C19H40	0.55
n-C20H42	0.79
n-C21H44 + Pyrn	2.48
n-C22H46	2.05
n-C23H48	1.95
n-C24H50	3.18
n-C25H52	3.06
n-C26H54	2.73
n-C27H56	
n-C28H58	
n-C29H60	
n-C30H62	
n-C31H64	
n-C32H66	0.24
n-C33H68	
n-C34H70	
n-C35H72	
n-C36H74	
Benz(a)anthracene	<0.01
Chrysene	<0.01
Benzo(b,j)fluoranthenes	0.01
Benzo(k)fluoranthene	0.01
Benzo(a)fluornathene	0.02
Benzo(e)pyrene	0.02
Benzo(a)pyre	0.01
Dibenz(a,j)anthracene	<0.01
Indeno(1,2,3-cd)pyrene	0.05
Dibenz(a,c/a,h)anthracenes	0.01
Benzo(ghi)perylene	0.08

TABLE A-24. COMPARISON OF ORNL RESULTS WITH NBS DATA FOR PAH  
ANALYSIS OF NBS SRM 1650 DIESEL EXHAUST PARTICULATES

<u>Constituent</u>	<u>ug/g</u>	
	<u>NBS</u>	<u>ORNL</u>
2-Nitrofluorene	0.27	0.4
9-Nitroanthracene	-	0.5
Benz(a)anthracene	6.5 ± 1.1	4.5
Chrysene	22	24
1-Nitropyrene	19 ± 2	2.7
Benzo(b/j)fluoranthenes	-	7.1
Benzo(k)fluoranthene	2.1	2.4
Benzo(a)fluoranthene	-	0.8
Benzo(e)pyrene	9.6	6.6
Benzo(a)pyrene	1.2 ± 0.3	1.4
Dibenz(a,j)anthracene	-	1.3
Indeno[1,2,3-cd]pyrene	2.3	6.3
Dibenz(a,h/a,c)anthracenes	-	1.2
Benzo(ghi)perylene	2.4 ± 0.6	6.5

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